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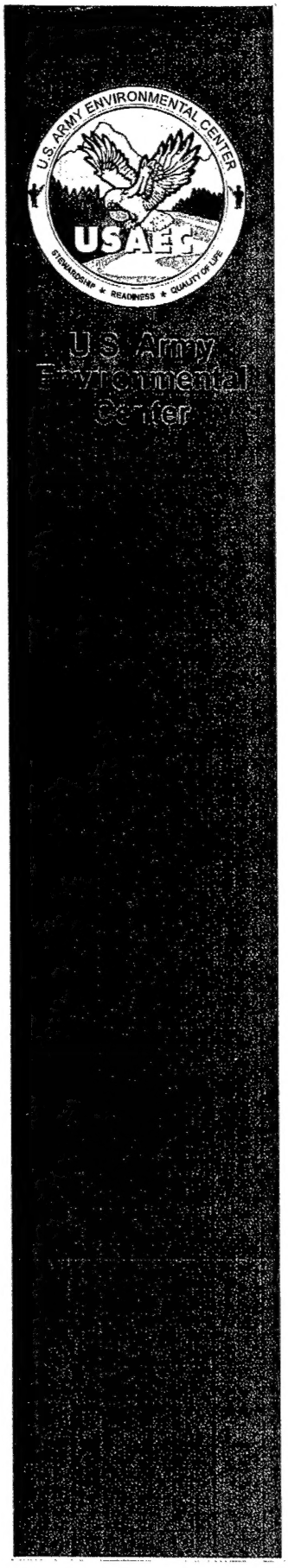

RESULTS OF THE TEAR GAS FATE AND EFFECTS STUDY

Volume I of II

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
Pollution Prevention and Environmental Technology Division
Aberdeen Proving Ground, Maryland 21010-5401

Prepared by
Tennessee Valley Authority
Environmental Research Center
Muscle Shoals, Alabama 35662-1010

June 1999

TVA Contract No. RG-99802V
Report No. SFIM-AEC-ET-CR-98027

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Volume I of II

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POC: A. J. Walker

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Fate, transport, and effects of CNS Tear gas in contaminated soils.

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This document describes the results of a study examining the environmental processes which effect of CNS tear gas and fate of the tear gas as it moves through soil. The study examines both the general properties of CNS tear gas as well as how these properties effected a CNS burial site at the Federal Laboratories No. 3 Plant near Saltsburg, Pennsylvania. The report also provides specific recommendations for remediating the Saltsburg site.

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EXECUTIVE SUMMARY

Although the Department of Defense (DoD) has sites in which the soil may be contaminated with CNS tear gas, very little data are available which describe the fate of tear gas in soil or on the environmental processes which affect CNS tear gas as it moves through soil. To address this problem, the United States Army Environmental Center (USAEC) contracted with the Tennessee Valley Authority (TVA) to conduct a three-phase study to examine the fate, transport, and effects of CNS tear gas in a drum burial site located on property owned by TransTechnology Corporation near Saltsburg, Pennsylvania. The drum burial site has been designated Area 15A and is located within the confines of a production facility referred to as Federal Laboratories Plant No. 3. Although the data collected are specific to Area 15A, the data obtained should provide insight into the behavior of CNS tear gas at other sites.

This project was conducted in three phases. Phase I involved the review of existing site characterization documents and feasibility studies. Also in Phase I, Direct Sampling Ion Trap Mass Spectrometry (DSITMS) was assessed to determine if it could be used to rapidly analyze the CNS tear gas components in groundwater and soil, and the use of a borehole flowmeter was demonstrated in several wells at Area 15A. A borehole flowmeter is an instrument which measures groundwater flow in wells.

Phase II consisted of the determination of behavioral characteristics of the three components of CNS tear gas, chloroform, chloropicrin, and phenacyl chloride in soil. Information developed in Phases I and II of the study were used in Phase III.

Phase III consisted of three tasks: 1) developing and executing hydrogeologic simulations to determine the effect of soil remediation on the natural restoration of the bedrock aquifer beneath the contaminated soil, 2) evaluating remedial strategies for disposition of the soil and groundwater contaminated by CNS tear gas, and 3) executing simulations of several injection and recovery system scenarios to develop an optimal system that can be used for delivering additives for *in-situ* remediation of the contaminated soil.

Volume I of this document summarizes the results and conclusions of all three phases of this study. A full description of the Phase II work is also provided in Volume I. Volume II contains full descriptions of all the work accomplished in Phases I and III of this study.

The CNS was buried at the Area 15A site just after World War II. Just prior to the burial, the DoD found that it had a surplus of CNS tear gas in its inventories. To dispose of this surplus material, the materials were sold to various private companies including a company called Federal Laboratories. Most of the surplus CNS purchased by Federal Laboratories was disposed of by open burning; however, an estimated 300 to 1,700 drums of CNS were buried at the Area 15A site. The Area 15A burial site is now the subject of an environmental investigation being conducted by TransTechnology Corporation, the present owner of Plant No. 3 and the successor-in-interest to Federal Laboratories. At this time, TransTechnology Corporation is continuing its efforts to find solutions to the contamination problem.

Federal Laboratories Plant No. 3 is located on a hillside which generally slopes to the west-southwest. The land in the immediate area surrounding Federal Laboratories Plant No. 3 is used for mining, farming, residential development, recreation, and industrial development. Mining is a major industry in the area. Both abandoned and active underground mines are present in the general and immediate vicinity of the facility. The Area 15A drum burial site consists of about 3 meters of soil atop bedrock consisting of fractured and interbedded sandstone, shale, and thin coal seams. The overburden is a silty sandy soil. The drums were placed in trenches dug into the soil overburden to a depth equal to the top of the underlying bedrock.

A review of existing documents indicated that nearly 90% of all of the drums in Area 15A have deteriorated and much of the tear gas has migrated downward into the underlying bedrock. Groundwater from the Area 15A site discharges along bedrock outcroppings of the uppermost water-bearing stratum about 200 meters west of Area 15A. The groundwater is discharged as seeps which flow into a tributary of the Elders Run located just below the rock outcroppings. The groundwater from the seeps is contaminated with chloroform, but the contamination appears to be confined to this water-bearing stratum and does not appear to have migrated to lower stratum. Analysis of groundwater in wells located upgradient of the rock outcroppings

indicates that chloroform is the most persistent of the three compounds and poses the greatest risk for discharge.

To determine groundwater flow characteristics of the site, groundwater flow measurements were made over 165 discrete intervals in eight wells using the borehole flowmeter technology being demonstrated. The borehole flowmeter tests revealed that groundwater flow was dominated by a few thin preferential flow zones. This is typical of fractured sedimentary rock aquifers in which groundwater moves preferentially through a few hydraulically active fractures with only minor flow through the porous rock matrix. A detailed report of this work is provided in Appendix E.

To predict the rate of chloroform flow through the bedrock, a finite element computer model was used. The model assumed that the chloroform would be subject to adsorption and first-order degradation in fractured porous media beneath Area 15A. Two scenarios were evaluated:

- A no-action scenario in which it was assumed that no attempt would be made to actively remediate the site and that natural restoration would be permitted.

- A soil remediation scenario in which it was assumed that all of the soil overburden would be actively remediated to remove all of the contaminants by the year 2000 and that the bedrock aquifer would be allowed to undergo natural restoration.

Predictions were only slightly sensitive to fracture distribution but highly sensitive to chloroform degradation rate. Simulations using an estimated degradation half-life of 277 days for chloroform provided the best agreement with observed down-gradient seep samples. This figure was consistent with a 227-day half-life determined by laboratory analysis. The model analyses also indicated that the chloroform concentrations at the seeps discharge points have peaked and that the concentrations are expected to decline with time.

The most significant finding of the modeling effort was that attempts to remediate the soil overburden would have no impact on aquifer restoration time. With or without soil remediation, all of the chloroform should be degraded by the year 2050 and concentrations at

the discharge boundary should fall below the MCL of 10^{-4} g/L by the year 2010. Details of the bedrock aquifer modeling work are provided in the report provided in Appendix F.

A complete review of the available data indicates that the complex geology and soil properties of Area 15A make the site a poor candidate for active soil remediation. Consequently, Monitored Natural Attenuation is likely to be the best soil remediation option for the Area 15A site. This is likely because:

- Most of the CNS tear gas is no longer in the drums.
- There are difficulties associated with remediating contaminants diffused into the low permeable soil present at Area 15A.
- In the current setting, the tear gas components pose little risk to the environment and deed restrictions and institutional controls can prevent human exposure to the landfill area.
- Computer modeling of the site indicates that soil remediation will have essentially no impact on aquifer restoration time.

Since soil remediation may be deemed a desirable option by the parties involved, despite the findings above, a variety of options for remediating the soil overburden and underlying bedrock were investigated. *In-situ* approaches were emphasized due to the short-term risks and high costs associated with *ex-situ* methods.

Two options for remediating the soil overburden appear promising:

- Enhanced chemical/biological degradation
- Thermally enhanced solvent vapor extraction

Remediation of the underlying groundwater/bedrock was considered separately and will be discussed later.

The most promising soil remediation approach is enhanced chemical/biological degradation. This approach involves the addition of a carbon source and chemical base to the soil to enhance the natural rate of chemical and biological degradation of CNS components in soil. The carbon source would be added to enhance microbial growth. Of the available carbon

sources, methanol is recommended since its use would foster the growth of methylotrophs that degrade chloroform. Addition of the chemical base is expected to both increase the level of microbial activity and to enhance the degradation of chloropicrin and phenacyl chloride. Currently the level of microbiological activity at the site has ebbed because CNS degradation resulted in soil acidification. Addition of a base will neutralize this acid, thereby encouraging increased microbial activity. In addition, the base is expected to enhance the hydrolysis of chloropicrin and phenacyl chloride. The preferred base is ammonium hydroxide because it will stimulate the growth of nitrifying bacteria, which are capable of degrading chloroform.

Three methods of delivering additives to the soil were evaluated. These included: injection trenches, shallow injection wells, and infiltration galleries. Of these options, an infiltration gallery was found to be superior to the other options because it allowed higher influx rates and provided better distribution of additive in the soil. Modeling of the infiltration galleries indicate that 1.3 pore volumes per year of aqueous-based additive could be added to the soil overburden. This is an order of magnitude greater than alternatives relying on vertical wells or trench systems.

In addition, three additive recovery systems were evaluated: extraction trenches, vertical wells, and horizontal wells. Horizontal wells were found to be the best option based on predictions of a numerical model which indicated that over 80 percent of the additive introduced by infiltration would be recovered by a horizontal extraction well system at Area 15A. This was the highest recovery rate among the alternatives modeled. In comparing the injection and recovery scenarios above, emphasis was placed on hydraulic efficiency and minimization of offsite contamination. A detailed report providing the bases for selecting the injection and recovery system recommended above is provided in Appendix H.

The second best alternative for treating the soil overburden at Area 15A is thermally enhanced solvent vapor extraction. This treatment method involves the addition of a chemical base and hot air while mixing the soil with a large diameter vertical auger. A soil vapor extraction system will also be required to capture and dispose of volatilized contaminants. This strategy is relatively simple and can be completed in a relatively short time. Its main disadvantage is that some of the contaminants will not be destroyed and will have to be captured in off-gas and treated. More aggressive chemical oxidation or reduction methods were considered but were

not recommended since they would sterilize the soil and decrease microbial degradation. Most of the remaining options could not be implemented at Area 15A due to site characteristics or the nature of the contaminants.

In response to the Pennsylvania Department of Environmental Resources (PADER) concerns regarding the offsite migration of chloroform, TransTechnology Corporation. is currently developing a groundwater/bedrock remedial strategy. The goal of this strategy, referred to as the targeted pump and treat, is to prevent CNS contaminants in the groundwater from reaching the Elders Run by intercepting the groundwater and treating the contaminants prior to discharging the groundwater. To implement the strategy, an array of extraction wells will be installed to intercept the groundwater from the uppermost aquifer (Saltsburg Sandstone). The groundwater/bedrock strategies examined in this report were considered a means of augmenting TransTechnology Corporation's proposed pump and treat system, and emphasis was placed on insuring that these systems could be incorporated into the proposed pump and treat system.

Several methods for remediating the groundwater/bedrock or preventing further contaminant migration were examined. These include:

- Low permeability caps or slurry walls (to contain the contaminants)
- *In-situ* solidification (to isolate the contaminants)
- *In-situ* vitrification (to degrade contaminants)
- *In-situ* treatment (to degrade contaminants)
- Monitored natural attenuation

Of these options, monitored natural attenuation was considered the most attractive. Most of the remaining options cannot be implemented at Area 15A due to site characteristics or the nature of the contaminants. For example, containing the contaminants, either by capping the site or using barrier walls, would not be a practical option at Area 15A since the fractured nature of the bedrock beneath Area 15A and the resulting high hydraulic conductivity would make it exceptionally difficult to contain the contaminants. Similarly, the use of solidification would not be an appropriate option for this site since solidification is unable to effectively isolate volatile organic constituents like those found in Area 15A. Solidification refers to the

mixing of cementious materials using an auger. The technique is primarily used to isolate inorganic contaminants. *In-situ* vitrification was rejected as an option because of high cost and because it is still in the early stages of development.

Some of the remaining *in-situ* treatment methods would be effective if the contaminants were only in the groundwater. Unfortunately, the contaminants have become embedded in the fractured bedrock's internal pore space. Because the contaminants must overcome capillary pressures to escape the rock matrix, it will take a long time for the contaminants to diffuse out of the bedrock and into the groundwater where they can be treated. Modeling of the aquifer indicates that it may take about 50 years for degradation and groundwater movement to remove the existing chloroform from Area 15A's bedrock (Appendix F). Given this timeframe, it is difficult to justify any of the *in-situ* groundwater treatment strategies.

The *ex-situ* pump and treatment option proposed by TransTechnology Corporation is a viable option if the goal is limited to preventing contaminant migration. However, as with the *in-situ* treatment methods, e*x-situ* treatment of the groundwater is not likely to result in an enhanced remediation rate due to the presence of contaminants in the rock matrix. Consequently, the parties involved may wish to review the need for a pump and treat system.

To support the conclusions above, various properties of the CNS components and the site soil were compiled from documented sources or determined experimentally. Specific methods used in the experimental determinations are provided in Section 3.0. The tear gas component and soil characteristics are described in mathematical terms as various rates, coefficients, and constants in Section 4.0. The characteristics provide information useful in modeling the movement and persistence of the tear gas components in soil and groundwater and for recommending remedial strategies.

In addition to the work described above, the Oak Ridge National Laboratory (ORNL) was contracted to develop a rapid analysis method for the CNS components using direct sampling ion trap mass spectrometry (DSITMS). This method involved either the direct purge of discrete 40-ml samples of water or soil or direct (*in-situ*) analysis of groundwater in wells using a specially designed sampling probe. The detailed report of this method development is provided in Appendix D. Experiments revealed that chloroform and chloropicrin could be

analyzed in water or soil using a 3-minute analysis time. Detection limits in water are in the range of 5 ppb. Soil detection limits are higher. Phenacyl chloride was not considered suitable for *in-situ* sparge analysis because the required analysis time was 15 minutes and the sample had to be heated to 60°C.

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ABBREVIATIONS

C	Carbon
°C	Degrees Centigrade
^{14}C	Carbon 14
$CaCl_2$	Calcium Chloride
µCi	Microcuries
Cl^-	Chloride
cm/s	Centimeters per Second
CN	Phenacyl Chloride
CNS	The term CNS tear gas refers to the military version of tear gas with a composition of 24% phenacyl chloride, 38% chloropicrin, and 38% chloroform by weight. The origin of the abbreviation CNS could not be determined but is thought to stand for the mixture of the two active ingredients phenacyl chloride (CN) and chloropicrin (PS) with the symbols combined. It is believed that the symbol for chloroform is not present because this component is not an active component and is present only to promote volatility.
CO_2	Carbon Dioxide
CS	O-Chlorbenzylidene Malononitrile
CWS	Army's Chemical Warfare Service
DoD	Department of Defense
DNAPL	Dense Non-Aqueous Phase Liquids
DSITMS	Direct Sampling Ion Trap Mass Spectrometry
EPA	Environmental Protection Agency
ERC	Environmental Research Center
°F	Degrees Fahrenheit
FTE	Fate, Transport, and Effects
g	grams
µg	Microgram
g/cm^3	Grams per Cubic Centimeter
µg/L	Microgram per Liter
GC	Gas Chromatography
GC/MS	Gas Chromatography - Mass Spectrometry
°K	Degrees Kelvin
kPa	Kilopascal
L	Liter
µL	Microliter
lb.	Pounds
M	Molar
M^2/day	Meters Squared per Day
µL	Micrometer
MDL	Method Detection Limit
mg	Milligram
mg/Kg	Milligrams per Kilogram

ABBREVIATIONS (Continued)

mg/L	Milligrams per Liter
ml	Milliliters
mm	Millimeter
mM	Millimole
NaOH	Sodium Hydroxide
NO_3^-	Nitrate
ORNL	Oak Ridge National Laboratory
ppb	Parts per Billion
PETG	Polyethylene Terephthalate
QA	Quality Assurance
QC	Quality Control
rpm	Revolutions per Minute
TOC	Total Organic Carbon
TVA	Tennessee Valley Authority
SL	Specialty Laboratory
SVE	Soil Vapor Extraction
UL	Uniformly Labeled
U.S.	United States
USAEC	United States Army Environmental Center
USEPA	United States Environmental Protection Agency
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compounds

SECTION 1.0
INTRODUCTION

1.1 Background

Although the Department of Defense (DoD) has sites in which the soil may be contaminated with CNS tear gas, very little data are available which describe the fate of tear gas in soil or on the environmental processes which affect CNS tear gas as it moves through soil. To address this problem, the United States Army Environmental Center (USAEC) contracted with the Tennessee Valley Authority (TVA) to conduct a three-phase study to examine the fate, transport, and effects of CNS tear gas in the soils of the Federal Laboratories Plant No. 3 in Saltsburg, Pennsylvania. Although the data collected are specific to the site, the data obtained should provide insight into the behavior of CNS tear gas at other sites.

The Federal Laboratories Plant No. 3 site has been used for production purposes since World War II. Just prior to the United State' entry into World War II, the Federal Laboratories Plant No. 3 site, then owned and operated by Federal Laboratories, Inc., was selected by the Army's Chemical Warfare Service (CWS) as an incendiary bomb manufacturing and loading facility. Shortly afterward, the munitions production facility was constructed, and from December 1941 through the end of the Vietnam conflict, the facility was used to manufacture a wide variety of products for the military including incendiary bombs, tear gas, vomit gas, munitions, and numerous other pyrotechnic and non-lethal chemical weapons.

Following World War II, the Department of Defense found that it had a surplus of CNS tear gas in its inventories. To dispose of this surplus material, the CNS materials were sold to various private companies, including Federal Laboratories. At Federal Laboratories No. 3, the surplus CNS was commonly disposed of by open burning. However, an estimated 300 to 1,700 drums of CNS were buried at a site designated as Area 15A.

The Area 15A burial site is now the subject of an environmental investigation being conducted by TransTechnology Corporation, the present owner of Plant No. 3 and the successor-in-interest to Federal Laboratories. Several environmentally contaminated areas were identified at the Federal Laboratories site during an inspection by the U.S. Environmental Protection Agency

Region III Field Investigation Team in 1983 and 1984. At this time, TransTechnology Corporation is continuing its efforts to find solutions to the contamination problem.

1.2 Project Objective

The objective of this project was to obtain information about the behavior of soil-borne CNS tear gas components (phenacyl chloride, chloropicrin, and chloroform) and to determine their fate in soil.

1.3 Approach

This project was conducted in three phases. Phase I of the Tear Gas Fate and Effects project consisted of a review of existing site characterization documents for Area 15A. Also in Phase I, Direct Sampling Ion Trap Mass Spectrometry (DSITMS) was assessed by the Oak Ridge National Laboratory (ORNL) to determine if it could be used to rapidly analyze the CNS tear gas components in groundwater and soil. Although the DSITMS work was conducted by ORNL, the results of the DSITMS work are summarized in this report. In addition, borehole flowmeter technology was demonstrated by TVA during Phase I. The borehole flowmeter is an innovative site characterization technology that can be used to measure groundwater flow at discrete intervals in a well hole.

During Phase II, the TVA conducted a fate, transport, and effects study of CNS tear gas components in soil. The goal of Phase II was to obtain basic information about the behavior of soil-borne CNS tear gas. This information was used to model CNS behavior during Phase III. To the extent possible, Phase II was built upon published information. However, some laboratory study was required to provide a theoretical basis for any conclusions reached. Because CNS components tend to segregate in soil and have different chemical and physical properties, the study focused on the behavior of these chemicals as individual components as opposed to behavior as mixtures. CNS tear gas consists of a mixture containing 24% phenacyl chloride (CN), 38% chloropicrin, and 38% chloroform.

In Phase III, TVA used the data collected in Phase II to model the transport characteristics of CNS in soil and bedrock and to investigate the potential use of innovative technologies to remediate tear gas contaminated sites.

This document reports the results of the Phase II Fate, Transport, and Effects Study; summarizes the results of the Phase I DSITMS work, summarizes the results of the Phase I Borehole Flowmeter Demonstration; and provides a summary of the Phase III results. Full descriptions of the Phase I and III studies are provided in the appendixes of this report.

1.4 Schedule

A Gantt chart of project activities is provided in Table 1-1. The project began September 15, 1996, and was completed in March 1999.

ID	Task Name
1	**Phase I: Project Initiation**
2	PADEP-TransTech meeting - tech. demo. options
3	Intial review of documents
4	AEC-TVA meeting - AEC tech. demo options
5	**ORNL DSITMS method development**
6	**Technology Demonstration**
7	Develop hydrogeologic work plan
8	Approval for borehole flowmeter as tech. demo.
9	Conduct borehole flowmeter tests
10	Summarize borehole flowmeter test data
11	Develop draft report of technology demo
12	Submit draft tech. demo report
13	**Phase II: Fate and Effects Study**
14	**Soil Collection**
15	Complete draft Health & Safety Plan
16	Complete draft soil collection plan
17	Review of 1st draft plan by AEC
18	Receive additional information from AEC
19	Receive additional info from TransTechnology
20	Revise plan
21	Review of 2nd draft plan by AEC
22	Review of 2nd draft plan by TransTechnology
23	Obtain samples

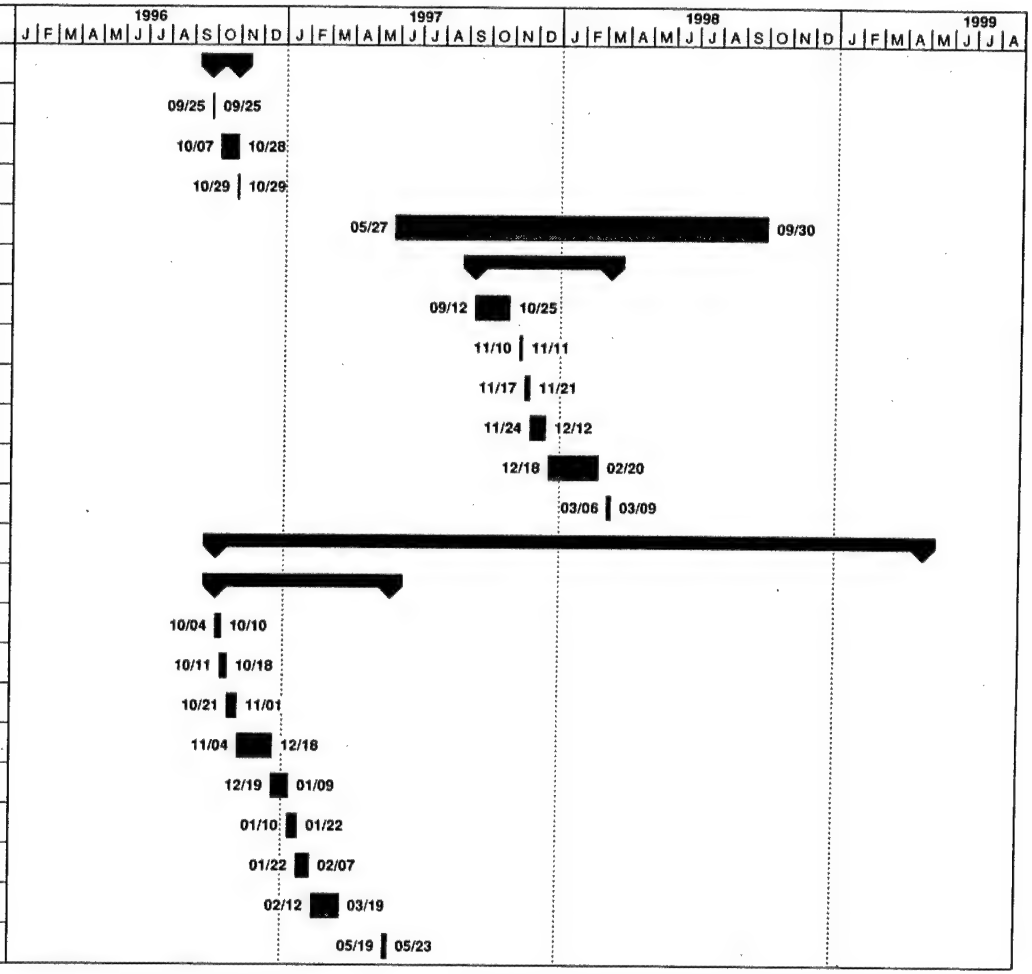


Table 1-1

Gantt Chart for the Tear Gas Fate and Effects Project

ID	Task Name	
24	**Second sampling and data collection**	11/14 11/14
25	Receive permission to do sampling	11/17 11/21
26	Collect contaminated samples for F&E study	11/17 11/21
27	Install data collection equipment	11/24 05/14
28	Collect precip, runoff, and well data	05/15 05/29
29	Compile and review data	06/01 06/05
30	Apply data to GW models	10/15 01/30
31	**Fate & Effects (F&E) Study**	01/30 03/11
32	Complete draft F&E test plan	02/13 03/18
33	Review of 1st draft plan by AEC	03/19 03/28
34	Review of 1st draft plan by TransTechnology	04/09 04/22
35	Revise 1st draft Test Plan	04/23 04/23
36	Review of 2nd version by PADEP	03/02 04/23
37	Finalize 2nd Version of Test Plan	04/24 04/24
38	Develop 3ed version of Test Plan	04/27 05/08
39	Submit 3ed version of Test Plan	05/11 06/08
40	Receive comments from AEC	06/09 06/09
41	Revise 3ed version of Test Plan	04/24 07/31
42	Submit final version of Test Plan	05/27 08/01
43	Synthesis	09/01 11/13
44	Soil analysis	03/11 09/11
45	Sorption	03/06 03/12
46	Degradation	
47	Transport	

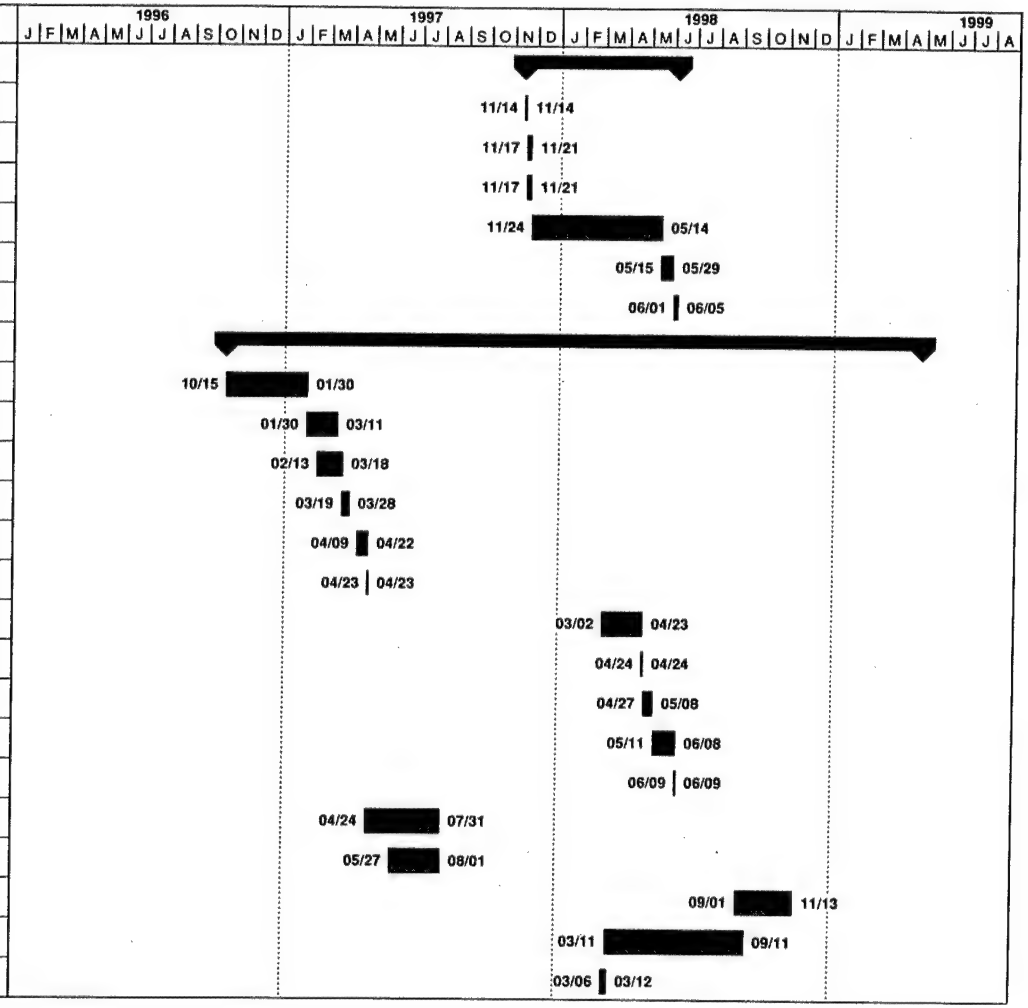


Table 1-1 (Continued)

Gantt Chart for the Tear Gas Fate and Effects Project

ID	Task Name	
48	Viscosity	02/17 – 03/02
49	Volatilization	03/06 – 03/12
50	Assemble all F&E data for use in models	09/14 – 09/14
51	Data interpretation	11/16 – 12/15
52	Draft F&E report	03/04 – 03/31
53	AEC review of draft report	04/01 – 04/14
54	Final F&E report	04/15 – 04/28
55	**Phase III: Remedial Alternatives**	
56	Identify remedial alternatives	12/03 – 09/30
57	Determine advantages and limitations of rem. alt.	10/19 – 10/30
58	Conduct initial screening of rem. alt.	11/13 – 11/30
59	Run MODFLO to optimize injection/recovery system.	12/01 – 12/14
60	Conduct final screening of remedial alternatives	12/15 – 01/11
61	Draft report of rem alt findings and recommend.	02/04 – 03/31
62	AEC review of draft report	04/01 – 04/21
63	Final report of rem. strategy recommendations	04/22 – 05/12

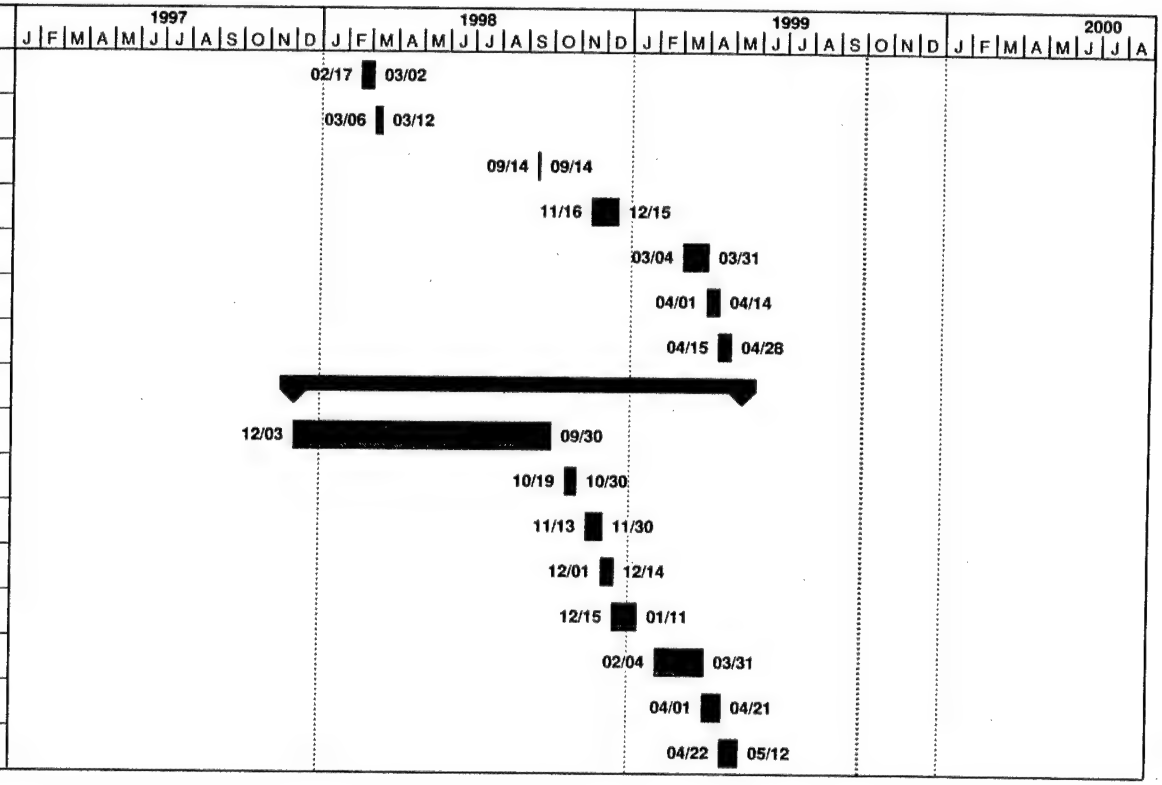


Table 1-1 (Continued)

Gantt Chart for the Tear Gas Fate and Effects Project

ID	Task Name
64	**Model Development**
65	Hydrogeological review of existing documents
66	Select porous media GW flow model
67	Develop porous media GW flow model
68	Run porous media GW flow model
69	Select fractured bedrock model
70	Develop fractured bedrock GW flow model
71	Select boundary conditions for fractured runs
72	Run fractured GW flow model
73	Summarize model runs output
74	Write draft report of both GW flow models
75	Submit draft report of GW flow models
76	Receive comments from AEC
77	Write final report of GW flow model work

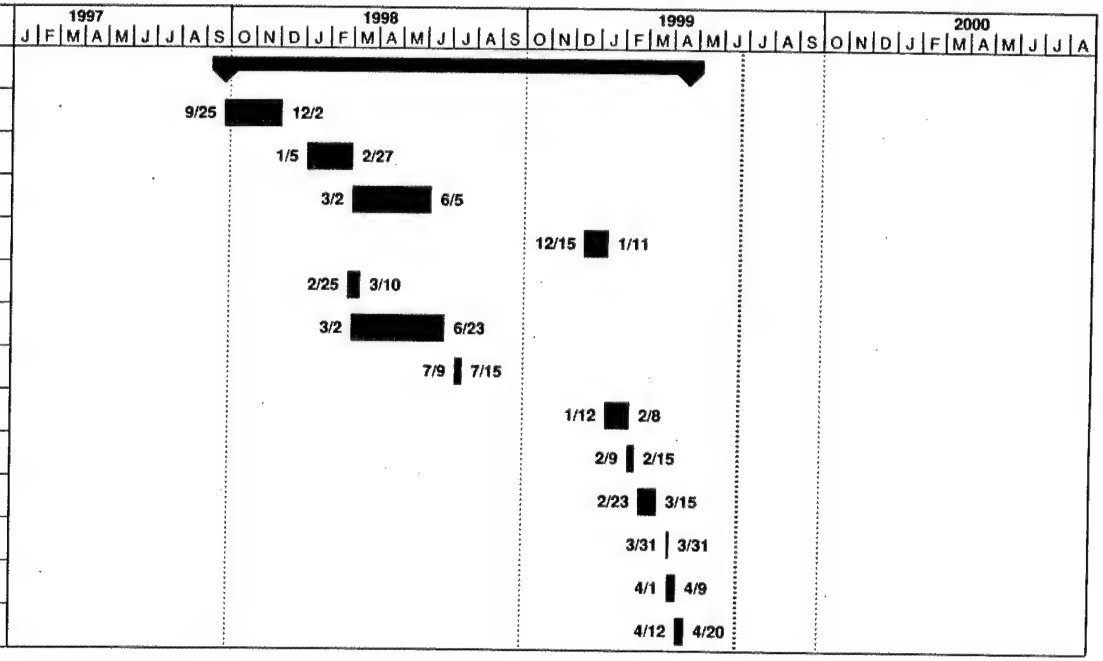


Table 1-1 (Continued)

Gantt Chart for the Tear Gas Fate and Effects Project

SECTION 2.0
SITE DESCRIPTION [Ref. 1]

2.1 Location of Federal Laboratories Plant No. 3

Federal Laboratories Plant No. 3 is located in Conemaugh Township, Indiana County, Pennsylvania. The facility is approximately 3 miles east of the town of Saltsburg and 1-1/2 miles north of the town of Tunnelton (Figure 2-1). The facility is approximately 2 miles north of the Conemaugh River. Manufacturing activities at the facility have occurred on approximately 35 acres adjacent to State Road 3003, commonly referred to as Tunnelton Road.

2.2 Description of Federal Laboratories Plant No. 3

Federal Laboratories Plant No. 3 is located on a hillside which generally slopes to the west-southwest. The land in the immediate area surrounding the plant is used for mining, farming, residential development, recreation, and industrial development. Mining is a major industry in the area. Both abandoned and active underground mines are present in the general and immediate vicinity of the facility. Dairy farming is the primary farming activity in the area, and farm use constitutes approximately 50% of land use in the immediate vicinity of the site. Most farms are located north, east, and southwest of the facility. Residential sites are located to the north and northeast. These residences tend to be widely spaced and surrounded by farms. As of June 1991, a nine-hole golf course was located approximately 2 miles northwest of the site. Two additional recreational projects are in the developmental stages, one approximately 4 miles west of the site and another approximately 2 miles south of the site. Little industry exists in the immediate vicinity of the facility.

Conemaugh Township, including the village of Tunnelton, has a population of 2,448 residents (1990 census). There are approximately 230 people living within a 1-mile radius of the site and approximately 2,050 people within a 3-mile radius of the site.

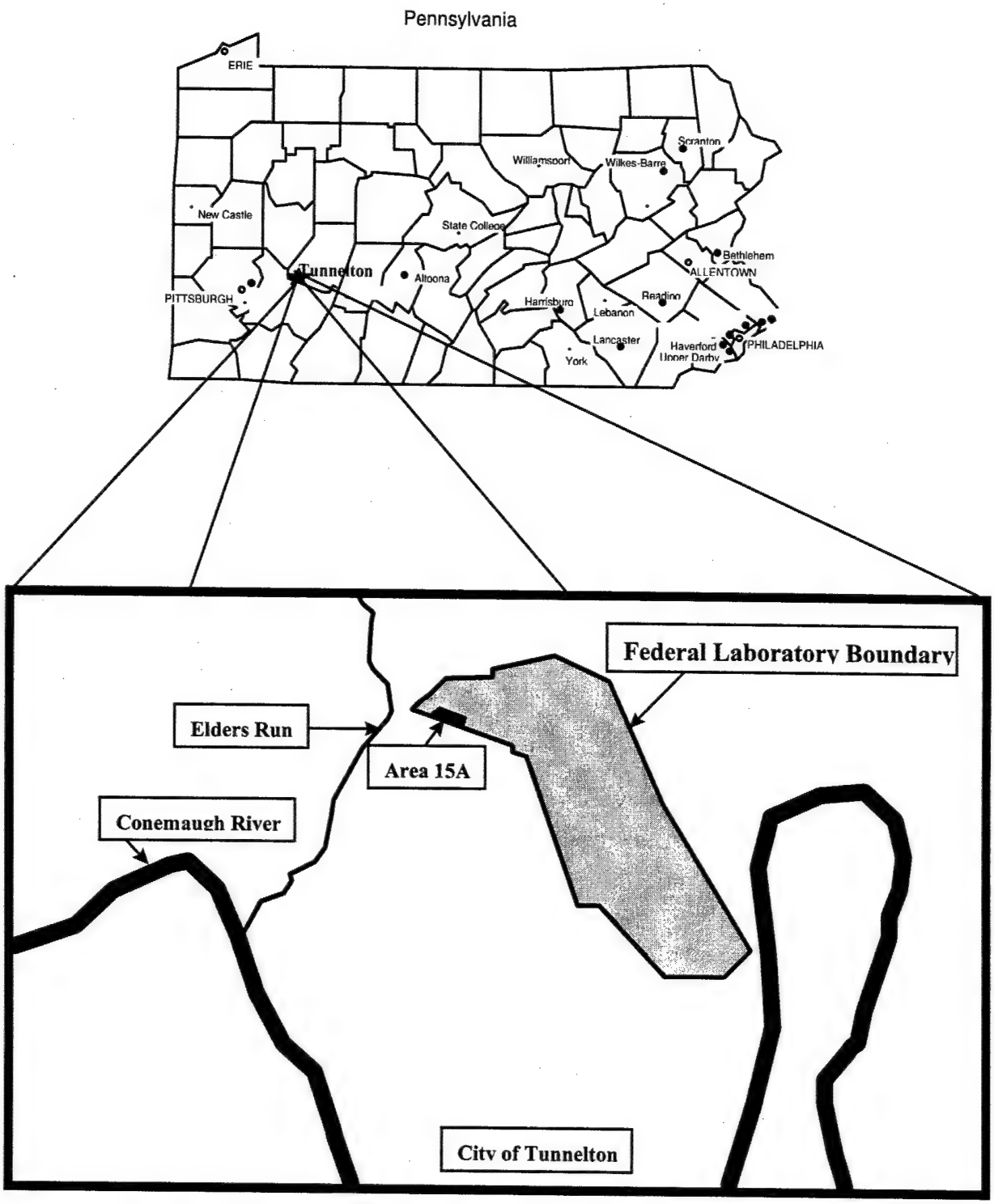


Figure 2-1

Location of Federal Laboratories Plant No. 3

2.3 History of Federal Laboratories Plant No. 3

Federal Laboratories, Inc., began operating in 1923 and quickly became the nation's leading manufacturer of tear gas for military use. In the months before the United States' entry into World War II, the U.S. Army's Chemical Warfare Service (CWS) identified three sites for manufacturing and loading incendiary bombs. One of these three facilities was to be owned and operated by Federal Laboratories, Inc. The facility in Saltsburg was designated Plant No. 3 because it was the third facility that Federal Laboratories operated in western Pennsylvania. During World War II, incendiary ordnance, tear gas grenades, and bursters were produced at the Saltsburg facility.

Following World War II, Federal Laboratories continued to supply tear gas to the United States as part of the Department of State's training program for newly emerging nations. During the Korean and Vietnam conflicts, Federal Laboratories continued to supply tear gas products, smoke grenades, and various incendiary products. These pyrotechnic products were principally smoke generators containing phenacyl chloride (CN) and o-chlorbenzylidene malononitrile (CS). Other operations at the Federal Laboratories facility included punching and stamping of stainless steel plates in addition to cadmium and chromium plating.

In 1947, Breeze Industrial Products, also known as Breeze Clamp, moved to the facility. Presently, Breeze Industrial Products operates its own building across from the former Federal Laboratories on the west side of State Route 3003, commonly referred to as Tunnelton Road.

In 1982, TransTechnology Corporation purchased Breeze Corporation, the parent corporation to Federal Laboratories. Federal Laboratories later merged into TransTechnology Corporation. As a result of this merger, TransTechnology Corporation assumed all of Federal Laboratories' corporate assets as well as its liabilities. All Federal Laboratories assets were sold to Mace Security International in 1994.

2.4 History of Contaminants at Federal Laboratories Plant No. 3

The kinds of wastes generated at the No. 3 plant have included cutting and lubricating oils, degreasing agents, heavy metals, and wastes containing various tear gas agents. The CNS wastes were generated after World War II when surplus CNS was shipped to Federal Laboratories. At that time, the excess CNS was disposed of both by open burning and on-site burial. It has been estimated that 300 to 1,700 drums of CNS are buried at the Federal Laboratories Plant No. 3 in the western portion of the property now known as Area 15A. The burial site is approximately 150 feet wide by 650 feet long.

The available evidence suggests that the buried CNS drums are leaking. Test pits in the burial area have indicated the drums are in a rusted and deteriorated condition. Furthermore, groundwater contamination consistent with CNS contamination has been detected at the Saltsburg facility as well as in surface water draining into Tributary B of the Elders Run which flows into the Conemaugh River (Figure 2-2). It is not believed, however, that the contaminants have migrated to any municipal or private water supplies. Contaminants detected in Tributary B include chloropicrin and chloroform. These contaminants are highly volatile and have distinctive odors recognizable at relatively low concentrations.

2.5 Site Characteristics at Federal Laboratories Plant No. 3

2.5.1 Climate

Indiana County has a continental climate with warm humid summers and cold winters. Prevailing winds, from the west and southwest, bring most of the major pressure systems affecting the area. The average wind direction is from the southwest (south 72° west).

Regional precipitation data (1962 to 1992) indicate an average annual precipitation of 36.4 inches. The maximum monthly precipitation rate was 11.05 inches (November 1985). The minimum monthly precipitation was 0.16 inch (October 1963). Annual precipitation for Tunnelton ranges from 40 to 44 inches. Temperature data indicate an annual average temperature of 52°F. Monthly highs average 77°F in July. Monthly lows average 11°F in January.

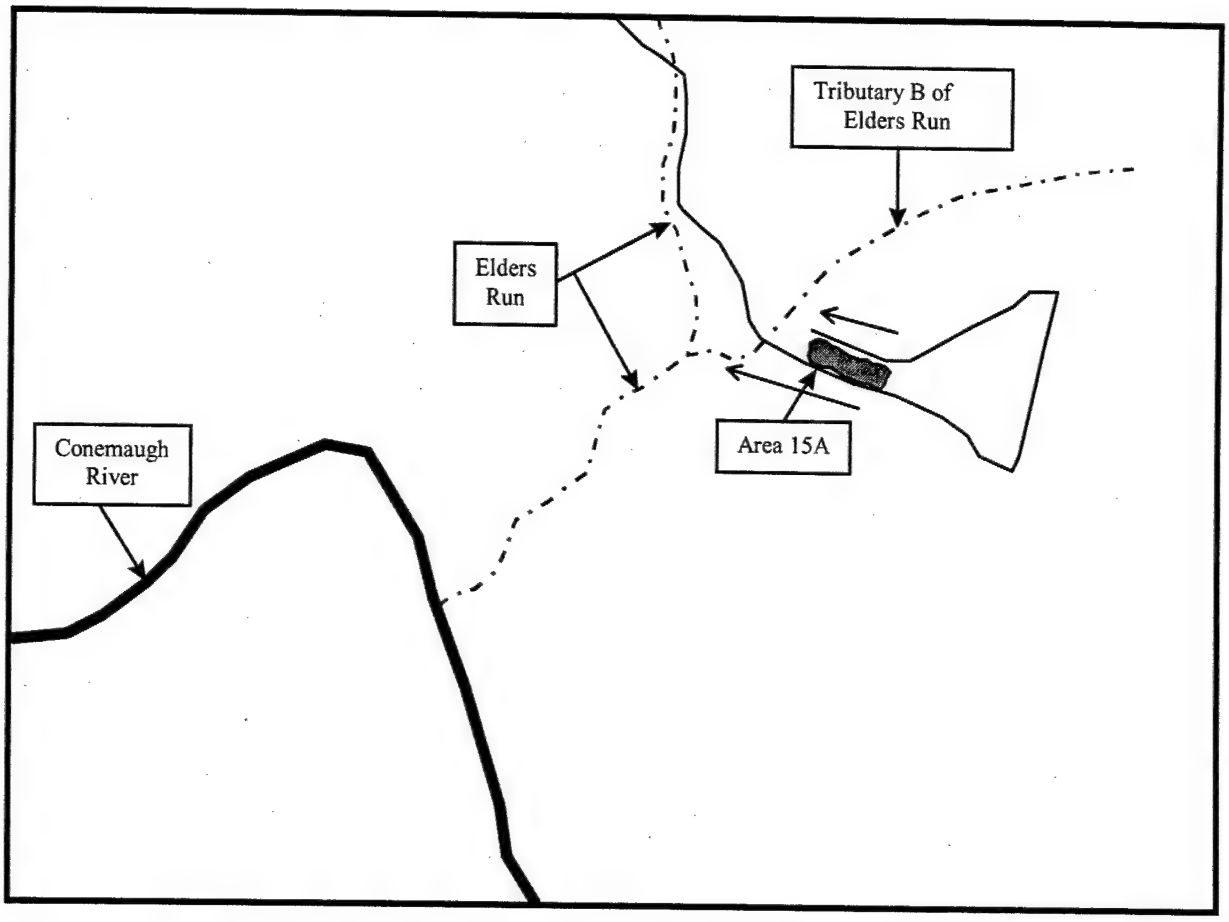


Figure 2-2

Surface Drainage from Area 15A

2.5.2 Regional and Local Geology

The Federal Laboratories Plant No. 3 is located within the Pittsburgh Plateaus Section of the Appalachian Plateau Physiographic Province. Geologic strata under the facility belong to the Pennsylvanian Age Glenshaw Formation of the Conemaugh Group. The Ames Limestone and Harlem (Friendsville) Coal form the upper boundary of the Glenshaw Formation while the Upper Freeport Coal defines its base. Water-bearing zones within the Glenshaw Formation include the Saltsburg, Buffalo, and Mahoning Sandstones. These units are subject to stratigraphic variation both laterally and vertically and consist of cyclic sequences of sedimentary rocks. Structural contours, based upon the elevation of the Upper Freeport Coal Seam, indicate that regional geologic structures consist of a series of northeast-southwest trending anticlines and synclines.

The active operations at the facility are located on the southeastern flank of the Jacksonville Anticline. This anticline plunges gently to the southwest in this area. Strata on the southeastern flank gently dip to the southeast at approximately 3 degrees. The anticlinal axis traverses the property in the vicinity of Area 15A, and the extreme northwestern portion of the site is located on the anticline's northwest flank.

2.5.3 Topography

The entire Federal Laboratories facility is located on a hillside which generally slopes to the west-southwest (Figure 2-2).

Surface drainage from the facility is intercepted by three unnamed tributaries:

- Tributary A of Elders Run which flows north to south through the central portion of the facility and collects the majority of the drainage from the site.

- Tributary B of Elders Run drains the westernmost portion of the property adjacent to Area 15A.

- A tributary draining the southern portion of the facility to the Conemaugh River.

2.5.4 Soil Type

Indiana County soil survey maps indicate that the former disposal areas are located in soils of the Brinkerton, Gilpin, and Wharton Series. Soil identification tests conducted during an environmental site assessment indicate Area 15A contains soils of the Wharton Series. The Wharton Series is typically located on gently sloping, broad hilltops and benches. The series consists of moderately well-drained residual soils developed from shale.

Other soil types that could be present are the Brinkerton Series, which is generally located in gently sloping valleys and consists of poorly drained soils developed from materials eroding from adjacent uplands, and the Gilpin Series which consists of moderately deep, well-drained soils developed from shale and sandstone bedrock.

2.5.5 Surface Waters

The Federal Laboratories site has three distinct drainage basins. Drainage Basin I runs through the northwestern portion of the Federal Laboratories property into Tributary B of Elders Run. The Basin I has an approximate surface area of 150 acres and contains Area 15A. Drainage Basin II flows from north to south through the approximate center of the property and receives the majority of the surface drainage from the Federal Laboratories site. Basin II has an approximate surface area of 726 acres and ultimately flows into Elders Run. Drainage Basin III drains into the unnamed creek that flows into the Conemaugh River. Basin III has an approximate surface area of 393 acres. Discharge from this Basin III is generally limited to a portion of the runoff from Area 17.

An impoundment is located immediately north of the eastern portion of the facility's operations area on one of the streams. This impoundment has been present for many years and currently is used to supply the water to a firewater storage tank and non-potable water system.

2.5.6 Groundwaters

Geologic information, obtained during a site investigation, identified Saltsburg Sandstone as the first continuous water-bearing zone beneath the Federal Laboratories facility. Buffalo Sandstone was identified as the first water-bearing zone underlying the Saltsburg Sandstone.

Under the eastern section of the facility, the groundwater associated with the Saltsburg Sandstone flows from the northeast to the southwest. This flow direction generally follows local topography but is also somewhat influenced by regional geologic structure. Potentiometric surface contours steepen in the vicinity of the Tributary B which flows through the northwestern portion of the site's property. In the site's western portion near Area 15A, the groundwater flows generally from northeast to southwest.

The groundwater flow direction within the Buffalo Sandstone is to the southeast in the eastern section following regional geologic structure. The western section of the site adjacent to Study Area 15A is located along the crest and on the northwestern flank of the Jacksonville Anticline. Groundwater flow direction within the Buffalo Sandstone in this area flows nearly east-west, reflecting this structural change in direction of regional dip.

2.5.7 Groundwater Contamination

The extent of groundwater contamination within the Saltsburg Sandstone in the vicinity of Area 15A has been defined.[Ref. 1] Contaminant migration is controlled by groundwater flow which is to the west-southwest. Wells located up-gradient to Area 15A contained no volatile organic compounds (VOCs) or only minor amounts of chloroform.

Wells located down-gradient, in the west and southwest, contain contaminants. Between June 1995 and January 1996, the maximum contaminant levels in the wells down-gradient from Area 15A were:

- 36 mg/L phenacyl chloride[Ref. 2]
- 680 mg/L chloroform[Ref. 2]

- 53 mg/L chloropicrin (no chloropicrin has been detected in the wells since June 1995)[Ref. 3]

Groundwater flow from these wells is to the west-southwest toward the stream valley leading to Elders Run. The Saltsburg Sandstone outcrops along these valley walls at an approximate elevation of 1,130 feet thus delineating the extent of contaminant migration to the west of Area 15A. Contaminants (chloropicrin and chloroform) have been detected in the Tributary B into which this basin drains. These contaminants are readily detected by their distinctive odors.

The vertical extent of contaminant migration appears to be generally limited to the Saltsburg Sandstone in the vicinity of Area 15A although sampling below the Saltsburg has been limited to just three wells completed in the underlying Buffalo Sandstone. In two instances VOCs have been detected in Buffalo Sandstone monitoring wells near Area 15A. Low concentrations of chloroform were detected in this formation on two occasions from October 1987 through July 1992.

In summary, groundwater contamination in the vicinity of Area 15A has been primarily limited to the Saltsburg Sandstone. Groundwater related to the Buffalo Sandstone formation has been largely unaffected. The Saltsburg Sandstone groundwater typically discharges to the surface as an intermittent seep or seeps into the Tributary B adjacent to Area 15A. A water supply inventory conducted in 1985 indicates that no domestic water supply wells exist within the contaminated water-bearing zones defined at the facility.

2.6 Location of TVA Facilities

Scientific research connected with this project was conducted at TVA's Environmental Research Center (ERC) located within the TVA Reservation near Muscle Shoals, Alabama. The TVA Reservation is located in the northwest corner of Alabama just north of the city of Muscle Shoals, in Colbert County, along the banks of the Tennessee River. The city of Muscle Shoals is located approximately 65 miles west of Huntsville, Alabama; 115 miles south of Nashville, Tennessee; 110 miles north of Birmingham, Alabama; and 150 miles southeast of Memphis, Tennessee.

SECTION 3.0
SAMPLING AND TEST PLANS

3.1 Introduction

Although the DoD may have sites where CNS tear gas contamination may be present, little data are available on the fate of CNS tear gas or on the environmental processes which affect CNS tear gas as it moves through soil. The goal of this project's sampling and test program was to obtain basic information about the behavior of soil-borne CNS tear gas in support of the tear gas fate, transport, and effects study conducted during Phase II. This information was used in Phase III to develop transport models to simulate the movement of CNS components though soil and groundwater.

The goals of the Phase II fate, transport, and effects study were met by characterizing the individual fate and transport characteristics of the three components of CNS tear gas, chloropicrin, phenacyl chloride, and chloroform, in soil. This was achieved by characterizing contaminated soil from the site and by exposing soil from the vicinity of Area 15A to each CNS component and then measuring the physical and chemical responses. Studying the behavior of individual components was desirable because these components tend to segregate and because they are often subjected to legal regulation based on their individual behavior. Measurement of these behavioral characteristics provided insight into:

- The physical and chemical nature of the soils at Saltsburg.
- The rate at which the components degrade.
- The amount of component retained on or in the soil.
- The volatilization characteristics of components in the soil.
- The potential for transport across the soil-gas interface.
- The interaction of environmental processes and their influence on the components.

A list of the specific chemical and physical characteristics sought is provided in Table 3-1.

Goals of the Phase II fate, transport, and effects study were accomplished in the tasks outlined in the project's Gantt chart (Table 1-1). These tasks included:

- Soil Sampling (Tasks 14 to 30) - in which a test plan for obtaining soil was written and the soil was obtained for laboratory use in the Phase II fate, transport, and effects study. Contaminated soil and groundwater samples were also collected for use in a direct sampling ion trap mass spectrometry (DSITMS) methods development study being conducted by ORNL.

- Preparing the Fate and Effects Test Plan (Tasks 32 to 42) - in which the project's test plan was written.

- Synthesis of Isotope-Labeled Chemicals (Task 43) - in which chemicals needed to conduct the project, but which were commercially unavailable, were produced.

- Soil Characterization Study (Task 44) - in which basic physical and chemical characteristics of the soil were determined.

- Soil Sorption Study (Task 45) - in which the degree to which CNS components were sorbed by the soil was measured. (The term sorption refers to adsorption to the surface of a material, absorption into the material, and precipitates which cannot be separated from the material.)

- CNS Degradation Study (Task 46) - in which CNS degradation and mineralization rates were measured.

- Transport Study (Task 47) - in which the soil-gas diffusion coefficient of each CNS component and the viscosity of chloropicrin was developed.

Table 3-1

List of Chemical and Physical Characteristics Measured in Each of the Project's Studies

Study	General Characteristic	Specific Characteristic
Soil Characterization	Chemical	CNS component concentrations in soil
		Soil pH
		Organic carbon content
	Physical	Moisture content
		Particle-size (percent rocks)
		Particle-size (percent sand, silt, and clay)
CNS Degradation	The rate of CNS components degradation in soil	Calculation of component half-life, $T_{1/2}$,for each CNS component in soil.
	Mineralization rate of CNS components	Rate of CNS component mineralization by fit to the three-half order Brunner-Focht equation.
Soil Sorption	Degree of sorption of CNS components by soil	A distribution coefficient, K_D, for each CNS component.
Volatility	Vapor density of CNS components	A vapor density, d, for each CNS component.
	Henry's Law Coefficient for CNS components	A Henry's Law Coefficient, h, for each CNS component.
Transport	Soil-gas diffusion of CNS components	Soil-gas diffusion coefficient, D_G, by the Millington-Quirk model for each CNS component.
	Viscosity of selected CNS components (chloropicrin)	Kinematic viscosity of chloropicrin
		Density of chloropicrin
		Viscosity of chloropicrin

- Volatility Study (Task 49) - in which parameters describing volatilization of CNS components were obtained.

- Data Interpretation (Task 51) - in which data gathered in the studies above were analyzed, interpreted, and modeled so as to develop a characterization of the soil and groundwater processes affecting the fate and transport of the CNS components and their interactions.

- Production of the Draft Report of the Tear Gas Fate and Effects Study (Tasks 52 to 54) - in which the results of the study were recorded.

Six of the ten tasks listed above (Tasks 44 to 49) were laboratory scale studies in which specific chemical or physical characteristics were measured or calculated. The remaining tasks were intended to provide support to the study tasks. The results of all the studies are summarized in this report of the Tear Gas Fate and Effects Study and submitted to the USAEC. All of the experiments were conducted at TVA's ERC. Individual test plans for each of the tasks listed above are provided in the sections that follow.

In addition to the Phase II test and sampling procedures described above, test and sampling procedures for DSITMS work (conducted by ORNL), the borehole flow meter demonstration, and the remedial strategies selection are more fully described in the following appendices.

Task	Appendix
DSITMS Method Development	D1 and D2
Borehole Flowmeter Demonstration	E
Remedial Strategies Selection	G

3.2 Sampling and Test Plans for Individual Tasks

3.2.1 Soil and Groundwater Sampling Plans

3.2.1.1 Overview

During the soil sampling tasks (Tasks 14 to 30), soil and groundwater samples were obtained from the vicinity of Area 15A for use in both the Phase II fate, transport, and effects study and a separate project being conducted by the Oak Ridge National Laboratory (ORNL). The goal of ORNL project was to develop methods for determining CNS concentrations in soil and groundwater using a DSITMS.

To support Phase II, one sample of contaminated soil was obtained from within Area 15A and eight uncontaminated (clean) soil samples were obtained from three areas located just outside of Area 15A (Table 3-2 and Figure 3-1). The areas from which the clean soil was obtained were designated Areas 1, 2, and 3. The soil samples were sent to TVA's ERC in Muscle Shoals, Alabama.

At the same time that the soil samples were collected for the fate, transport, and effects study, groundwater and soil samples were collected for use in a separate project conducted by the Oak Ridge National Laboratory (ORNL). ORNL used these samples to develop DSITMS analytical methods for determining CNS concentrations in soil and groundwater. The ORNL samples consisted of: one contaminated groundwater sample from monitoring well MWU-20, one uncontaminated groundwater sample from monitoring well MWU-15, one contaminated soil sample from Area 15A, and one uncontaminated soil sample from Area 1 (Table 3-2 and Figure 3-1). These samples were sent to ORNL's facility in Oak Ridge, Tennessee.

3.2.1.2 Soil Sampling Procedure

Soil collection was initiated in the most upgradient location and proceeded in the down-gradient direction. Prior to soil collection, any leaf and plant litter on the soil surface was cleared away. The soil sampling method of the uncontaminated soil varied with the depth of the sample collected. At sampling depths of 0 to 2 feet, fiberglass

Table 3-2

Soil and Groundwater Samples Collected from the Federal Laboratories Facility, Saltsburg, Pennsylvania

Sampling Location	Sample Identification	Sampling Depth (feet)	Minimum Quantity (lb)	Sample Container	Sample Preservation	Sample Used in Project Phase	Sampling Location Description
Area-1	Soil-1	0.5-2	18	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
	Soil-1A	0-2	18	Triple Bagged	none	ORNL Project	See Figure 3-1
	Soil-2	2-4	31	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
Area-2	Soil-3	0.5-2	18	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
	Soil-4	2-4	31	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
	Soil-5	4-6	18	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
Area-3	Soil-6	0-3	18	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
	Soil-7	3-6	18	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
	Soil-8	6-8	18	Triple Bagged	none	Phase II FTE[1] Study	See Figure 3-1
Area 15A	Soil-9	6-9.5	8	Teflon™ lined core (2)	cool on ice	ORNL Project	See Figure 3-1
	Soil-10	6-9.5	9	Plastic lined core (2+)	cool on ice	Phase II FTE[1] Study	See Figure 3-1
Groundwater-1	Uncontaminated monitoring well	Water Surface	4 liters 6-40 ml vials	1-L NM Amber Glass 6-40 ml vials	pH < 2 cool on ice	ORNL Project	See Figure 3-1
Groundwater-2	Contaminated monitoring well	Water Surface	4 liters 6-40 ml vials	1-L NM Amber Glass 6-40 ml vials	pH < 2 cool on ice	ORNL Project	See Figure 3-1

(1) FTE - Fate Transport and Effects

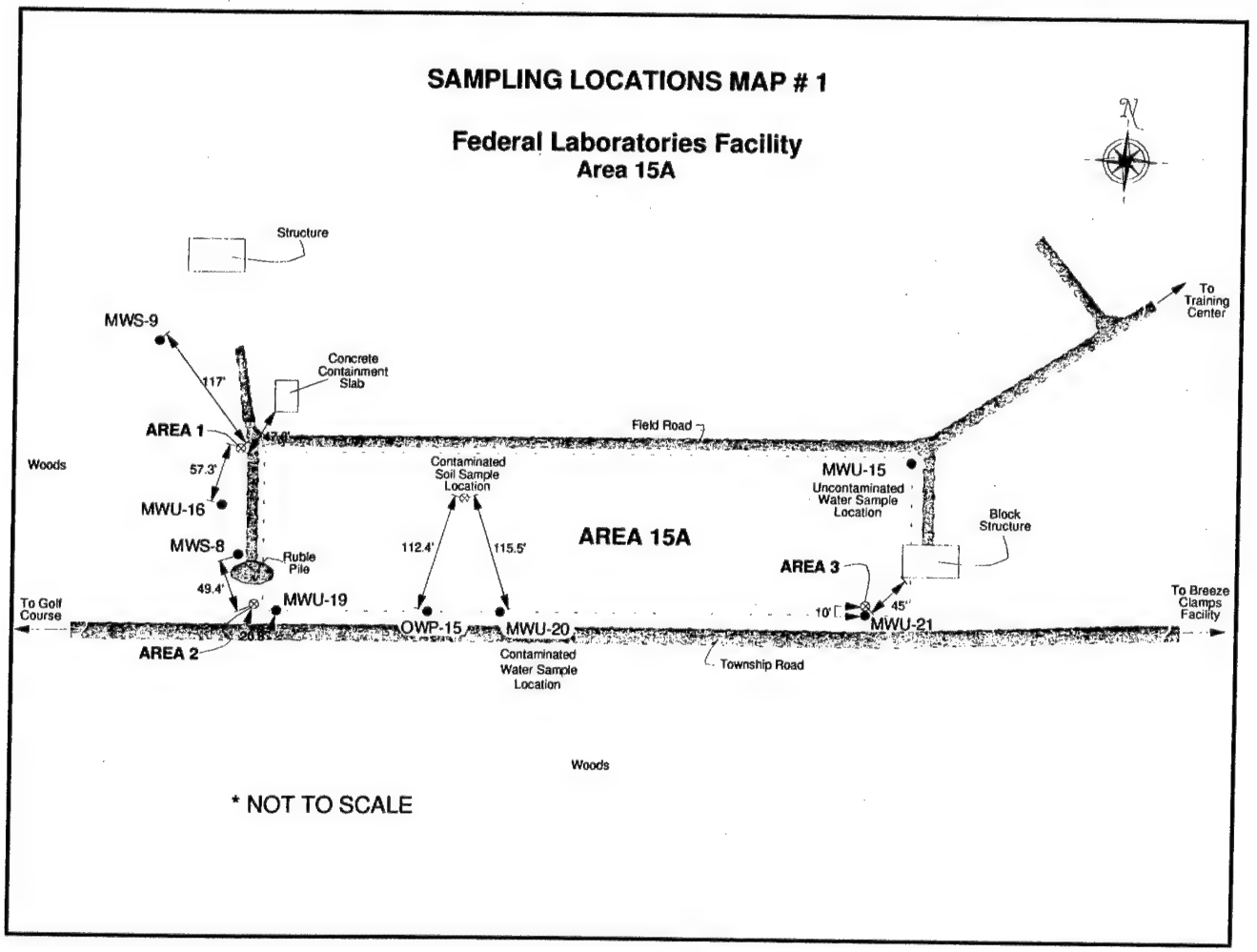


Figure 3-1

Sampling Locations Map #1

post-hole diggers were used. At sampling depths below 2 feet, a Little Beaver Earth Drill® with 6-inch flight metal augers was used. Once the desired depth was reached with the drill, the augers were removed and a hollow stainless steel bucket auger with a T-handle and extensions was inserted to retrieve the soil. Multiple bucket auger volumes were required to obtain the necessary quantity of uncontaminated soil. Any extra uncontaminated soil removed from each boring was placed back in the boring from which it originated when the soil collection was completed.

3.2.1.2.1 Uncontaminated Soil Collection Procedure

The uncontaminated soil collected was placed directly into a labeled plastic bag, triple bagged in large heavy duty plastic bags, and placed in cardboard boxes for transfer to ORNL in Oak Ridge, Tennessee, and to TVA in Muscle Shoals, Alabama. The uncontaminated soil was not preserved in any way. TVA personnel maintained custody of the samples from the time of collection until the samples were delivered to ORNL or TVA for use in the respective studies. A chain-of-custody record was maintained as required by TVA's Specialty Laboratory (SL) procedure SP-0001, "Sample Chain-of-Custody."

3.2.1.2.2 Contaminated Soil Collection Procedure Used for Phase II and Phase III

The one contaminated soil sample was collected with a Geoprobe® Macro-Core Sampler using clear plastic liners made of polyethylene terephthalate (PETG). This sample was analyzed for the physical characteristics required to do the Phase III modeling. The sampling device and liner were sterilized with ethanol and allowed to air dry prior to sample collection. After a contaminated soil sample had been retrieved from the ground, it was immediately prepared by: (1) cutting the top 6 inches and bottom 2 inches off, then (2) both ends of the liner were covered with Teflon™ tape and sealed with friction fit vinyl end caps (black denoted the bottom of sample, orange denoted the top), and finally (3) placed in an ice chest with a layer of cardboard separating the sample from ice to prevent sample freezing. Latex gloves were worn at all times when handling the samples. Any extra contaminated soil was placed in a 55-gallon, open-top metal drum and disposed by TransTechnology Corporation. The contaminated soil sample sent to TVA's ERC was delivered to Muscle Shoals, Alabama, within 72 hours of sample collection and refrigerated at 4°C until analyzed. TVA personnel maintained custody

of the samples from the time of collection until the samples were delivered to TVA. A chain-of-custody record was maintained as required by TVA's Specialty Laboratory (SL) procedure SP-0001, "Sample Chain-of-Custody." (Please note that volatiles can still be lost under the sampling conditions described, therefore, site characterization information should not be derived from this data.)

3.2.1.2.3 Contaminated Soil Collection Procedure Used to Collect Samples for the ORNL Study

Descriptions of the procedures used to collect contaminated soil for use in the ORNL study are provided in the "*Soil and Groundwater Sample Collection Plan*" provided in Appendix A.

3.2.1.3 Groundwater Sampling Procedure

Descriptions of the procedures used to collect groundwater for use in the ORNL study are provided in the "*Soil and Groundwater Sample Collection Plan*" provided in Appendix A.

3.2.2 Test Plan for the Soil Characterization Study

Each uncontaminated soil sample was characterized in terms of percent of the mass consisting of rocks, particle size distribution, organic carbon, and soil pH (Table 3-3). In addition, the contaminated soil sample was analyzed for CNS component concentrations, organic carbon, and soil pH (Table 3-3).

Upon receipt of the uncontaminated soil samples at TVA's ERC, each uncontaminated soil sample was passed through a 2-mm sieve, air-dried, ground, mixed, and stored. The soil samples were stored in either plastic containers or triple bagged in plastic bags. Any rocks that did not pass through the sieve were weighed, and the source sample containing the rocks was identified. All samples were processed and stored in the ERC building. Soil subsamples of the uncontaminated soil were taken from the main soil containers by dipping a beaker into the soil container and removing the subsamples to clean, labeled containers.

Table 3-3

Chemical and Physical Analysis for the Soil Characterization Study

Sample Type	Number of Samples	Preservative Added	Parameter Measured	Method[1]
Contaminated Soil	1	None	CNS component concentration	GC (AP-0046)
Contaminated and Uncontaminated Soil	9	None	pH	ASA Method 12-2.6
Contaminated and Uncontaminated Soil	9	None	Organic carbon	ASA Method 29-3.5
Contaminated Soil	1	None	Particle-size analysis	ASTM D422
Uncontaminated Soil	8	None	Particle-size analysis	ASA Method 15-5

(1) See Appendix B for details of methods and procedures.

3.2.3 Test Plan for the Synthesis of Labeled Chemicals

3.2.3.1 Overview

Four ^{14}C-labeled chemicals were considered for use in the CNS degradation study.

- Chloroform-^{14}C
- Chloropicrin-^{14}C
- Phenacyl chloride-ring-^{14}C
- Phenacyl chloride-carbonyl-^{14}C

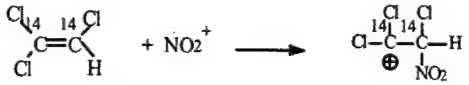
All four compounds were synthesized, but the labeled ring phenacyl chloride was used for determinations rather than labeled carbonyl phenacyl chloride. Consequently, the labeled carbonyl phenacyl chloride was not used. Chloroform-^{14}C was available commercially and was purchased from American Radiolabeled Chemicals Incorporated (St. Louis, Missouri). The other chemicals were synthesized at TVA's ERC. Estimates of the amount of chemical required for the study are provided in Table 3-4.

3.2.3.2 Synthesis of Chloropicrin- ^{14}C

General Method

Chloropicrin- ^{14}C was prepared by a microscale adaptation of literature procedures [Ref. 4] using trichloroethylene-1,2-^{14}C as the starting material, Equations 1-6. The trichloroethylene-1,2-^{14}C was purchased from Sigma Chemical Company (St. Louis, Missouri).

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons H_3O^+ + NO_2^+ + 2\,HSO_4^- \qquad (1)$$



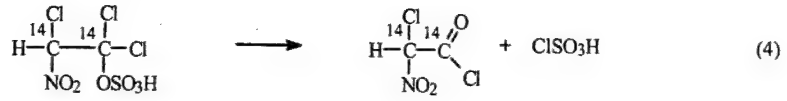
(2)

(3)

Table 3-4

Minimum Amount of ^{14}C Required to Conduct Laboratory Experiments

CNS Component	Study	Amount Required (μCuries)
Chloroform-UL-^{14}C	CNS degradation	24
	Total	24
Chloropicrin-UL-^{14}C	CNS degradation	24
	Total	24
Phenacyl Chloride-Ring-UL-^{14}C	CNS degradation	24
	Total	24
Phenacyl Chloride-Carbonyl-^{14}C	CNS degradation	24
	Total	24



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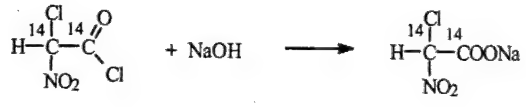

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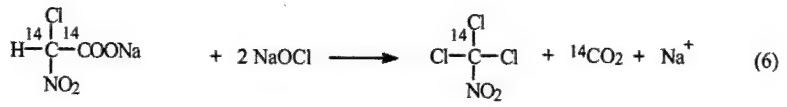


(6)

Procedure for the Production of Chloropicrin-^{14}C

A mixture of labeled and unlabeled trichloroethylene was prepared by adding 4.2 µl of trichloroethylene-1,2-^{14}C (500 µCi) to 0.04 ml of unlabeled trichloroethylene. In a 5-ml round bottom flask, the mixture containing trichloroethylene-1,2-^{14}C (0.05 mmole), trichloroethylene (0.45 mmole), and 62.5 µl of concentrated nitric acid (0.99 mmole) was cooled in an ice bath. Sulfuric acid (56 µl or 1.009 mmole) was then slowly added to the mixture, and the cooled mixture was stirred for 3 hours. An aqueous solution containing 40 mg NaOH (1.0 mmole) and 111 mg NaOCl (1.491 mmole) was then added to the mixture and allowed to stir overnight at room temperature. The resulting oil was separated from the aqueous solution and purified by capillary column chromatography at 200°C and a retention time of 1 minute. At 100% of theoretical yield, 7.67 mg (500 µCi) of chloropicrin-^{14}C may be produced from this mixture. An aliquot (1 µl diluted to 10 ml in acetone) was submitted to TVA's Specialty Laboratory for GC analysis (Table 3-5) to assess the purity of the final product. The retention time of the product was compared to the retention time of unlabeled reference material. Further verification of the identity of the synthesized product was made by performing GC analysis on a different column and comparing the retention time to that of unlabeled reference material. The final product was stored in a refrigerator.

Table 3-5

Chemical Analysis Required for the Chemical Synthesis

CNS Component Tested	Sample Type	Samples Required	Parameter Measured	Method [1]
Chloropicrin	Solution	1	Product Purity	GC (AP-0046)
Phenacyl Chloride-ring	Solution	1	Product Purity	GC (AP-0046)
Phenacyl Chloride-carbonyl	Solution	1	Product Purity	GC (AP-0046)

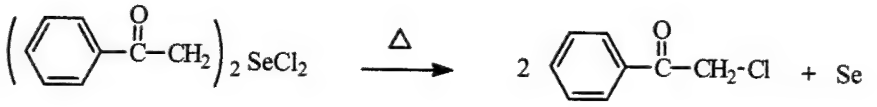
(1) See Appendix B for details on methods and procedures.

3.2.3.3 Synthesis of Phenacyl Chloride-Ring-UL-^{14}C and Phenacyl Chloride-Carbonyl-^{14}C

General Method

Phenacyl chloride-^{14}C was prepared by a microscale adaptation of literature methods[Refs. 5&6] using ^{14}C-labeled acetophenone as the starting material, Equations 7-8. Acetophenone-ring-UL-^{14}C (uniformly labeled) and acetophenone-carbonyl-^{14}C were purchased from Sigma Chemical Company. Selenium oxychloride was purchased from Aldrich Chemical Company (St. Louis, Missouri).

(7)



(8)

Procedure for the Production of Phenacyl Chloride-Ring-UL-^{14}C

In a microscale conical vial, 0.8 ml benzene, 50.6 mg non-labeled acetophenone (0.42 mmole), and 9 mg acetophenone-ring-UL-^{14}C (0.08 mmole, 500 μCi) were cooled in an ice bath. Selenium oxychloride (43.1 mg or 0.26 mmole) was slowly added and the mixture allowed to stand at room temperature for 2 hours. The precipitate was removed by filtration. Purification by pyrolysis of the precipitate gave phenacyl chloride-ring-UL-^{14}C. A review of the literature suggests the expected yield should be 50% the theoretical yield or 5.836 mg of phenacyl chloride-ring-UL-^{14}C (250 μCi). An aliquot (1 μl diluted to 10 ml in acetone) was submitted to TVA's Specialty Laboratory for GC analysis (Table 3-5) to assess the purity of the final product. The retention time of the product was compared to the retention time of unlabeled reference material. Further verification of the identity of the synthesized product was made by GC analysis on a different column and comparison of the retention time to that of unlabeled reference material. The final product was stored in a refrigerator.

Procedure for the Production of Phenacyl Chloride-Carbonyl-^{14}C

The procedure for the preparation of phenacyl chloride-carbonyl-^{14}C was identical to the procedure for phenacyl chloride-ring-UL-^{14}C preparation. However, 14.3 mg or 0.12 mmole acetophenone-carbonyl-^{14}C (500 µCi), 45.3 mg non-labeled acetophenone (0.38 mmole), 0.5 ml benzene, and 40.7 mg or 0.245 mmole selenium oxychloride were used as starting materials.

3.2.4 Test Plan for the CNS Degradation Study

3.2.4.1 Overview

The CNS Degradation Study was designed to determine two characteristics:

- The half-life of CNS components in soil
- The rate of mineralization of CNS components to carbon dioxide

Two experiments were conducted in this portion of the study. In the first experiment, soil-borne CNS components were incubated in volatile organic analysis (VOA) vials while the component concentrations were periodically measured. The component concentration data were used to determine component half-lives. In the second experiment, the rate of mineralization of the soil-borne CNS components was determined using ^{14}C-labeled CNS components to track the amount of carbon dioxide produced in VOA vials. The rate of mineralization was expressed by fit to the Brunner and Focht three-half order rate equation.[Ref. 7]

The experiment was conducted under aerobic conditions. Aerobic degradation was emphasized because:

- Most of the degradation occurring at Area 15A is thought to be occurring under aerobic conditions based on the existence of expected aerobic degradation by-products in groundwater (e.g., Castro). Relatively small anoxic regions likely exist, if only temporarily, in the contaminated soil overburden where oxygen has been depleted by degradative activity or where groundwater circulation is restricted.

- Chloropicrin and chloroform have been observed to degrade both aerobically and anaerobically. In pure (single organism) cultures, chloropicrin hydrolyzes to produce phosgene and nitrosyl chloride. Hydrolysis in the presence of light produces CO_2, Cl^-, and NO_3^-.[Ref. 8] Similarly, chloroform is oxidized to phosgene which then hydrolyzes to the bicarbonate ion.[Ref. 9]

- The heme protein P-450_{cam}, an important enzyme for xenobiotic detoxification in vivo, degrades chloroform and chloropicrin by reductive dehalogenation in pure cell cultures under aerobic conditions and with pure enzymes under reducing conditions.[Refs. 10,11,& 12]

- Ring-chlorinated acetophenones are known to degrade oxidatively via the Baeyer-Villiger oxidation[Refs. 13,14,&15] (although specific data on degradation of phenacyl chloride were not available).

3.2.4.2 Determination of Component Half-Life

In the half-life experiment, VOC vials containing soil spiked with chloropicrin, chloroform, or phenacyl chloride were incubated to determine the chemical half-life of each component in soil. The VOC vials were held for a period of time, then harvested for analysis of the component concentrations. Vials were harvested periodically until most or all of the component had dissipated. Component half-lives were calculated based on the amount of contaminant remaining in the soil. An outline of the experimental design is provided in Table 3-6. Although the experimental design called for the taking of samples at 2 weeks, 4 weeks, 8 weeks, 12 weeks, 16 weeks, and 6 months; the experiment was terminated at 6 weeks because the CNS components dissipated early in the observation period. The experiment was disassembled at that point and the remaining vials disposed of properly.

Table 3-6

Experimental Design for Component Half-Life Determination

Sample Period	CNS Component	Initial Soil Concentration (mg/Kg)	Replicates Per Sample Period	Analyses	Number of Samples
2 weeks	Chloroform	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Chloropicrin	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Phenacyl Chloride	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
				Subtotal	12
4 weeks	Chloroform	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Chloropicrin	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Phenacyl Chloride	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
				Subtotal	12
8 weeks[1]	Chloroform	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Chloropicrin	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Phenacyl Chloride	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
				Subtotal	12
12 weeks[1]	Chloroform	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Chloropicrin	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Phenacyl Chloride	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
				Subtotal	12
16 weeks[1]	Chloroform	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Chloropicrin	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Phenacyl Chloride	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
				Subtotal	12
6 months[1]	Chloroform	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Chloropicrin	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
	Phenacyl Chloride	100	3	Table 3-7	1 period X 3 replicates + 1 control = 4
				Subtotal	12
				Total	72

(1) In practice, the test was terminated after 6 weeks because the CNS components dissipated early in the observation period.

The procedure for determining half-life was as follows. A sufficient number of 40 ml VOA vials were acquired to provide three replicates of the treatment and one control per treatment to be harvested at each designated time interval. Each vial was filled with 25 grams of oven-dry soil and sufficient water was added to each vial to bring the soil-water potential to -33 kPa (15% moisture by volume). Soil-water potential is the amount of work necessary to detach the water from the soil matrix and is equal to the reduction in the potential energy of the water. Each of the three CNS components was added to its designated treatment and control vials, resulting in a concentration of 100 mg component per kg soil. After the addition of the target component, the vials were quickly capped and the contents well mixed.

The control at each planned sampling period consisted of a vial prepared using steam sterilized soil (121°C for 1 minutes) to which mercury (II) chloride was added for a concentration of 0.1 g per 100 g soil. This soil preparation was intended to prevent microbial degradation of the component. The control vials were prepared such that the loss of volatile components during the experimental set-up phase was comparable to component loss during the set-up of the treatment vials. In this way the controls were to provide a baseline concentration for each component after spiking and allow for a method to track the amount of component lost to volatilization over the course of the experiment. Every effort was made to minimize component loss through volatilization during experimental set-up. The openings in the vials were sealed with Teflon™-lined Mininert valve (24 mm-400 thread size) caps (Valco Instruments, Inc., Houston, Texas). This type of cap uses a valve to seal the septum. The septum was only exposed to the vial atmosphere during sampling or aeration. For example, after an aeration period (described in next paragraph), the valve was repositioned to make an air-tight seal. Therefore, had the septum become severely cored and leaked, the leakage only occurred during the short sampling period. Likewise, slow diffusion through the septum was dramatically reduced because a Teflon™ valve, that is never cored by the needle, was used to seal the vial during non-sampling or aeration periods. Furthermore, if it were suspected that the septum was leaking, even slightly, during the aeration period, the Mininert™ caps are designed such that the septum can be changed without breaching the integrity of the sample. In summary, the caps were equipped with a septum and valve to prevent loss of volatile components, yet allow periodic aeration of the sample via syringe.

After the vials were prepared, they were placed in a dark incubator in random positions. Incubator temperature was maintained at 25°C. The vials were aerated weekly for the duration of the incubation period by injecting several microliters of oxygen through the septum in each vial cap.

At each harvest interval, the soil in the three replicate treatment vials and the control vial was transferred to TVA's Specialty Laboratory for analysis. The soil was extracted with hexane according to the protocol in Appendix B-4 and analyzed for parent component by gas chromatography (GC), Table 3-7.

The component half-life, $T_{1/2}$, of each component was calculated as a function of the amount of component, M_t, remaining in the soil after time, t, by the following equation:

$$T_{1/2} = -0.693t / \ln\left(\frac{M_t}{M_0}\right) \qquad (9)$$

where M_0 is the initial mass of component in the soil.

3.2.4.3 Determination of Component Mineralization Rates

In this experiment, the mineralization rates for each CNS component were determined by measuring the amount of ^{14}C-labeled carbon dioxide ($^{14}CO_2$) produced. The experiments were designed similarly to those used to determine the half-life (Section 3.2.4.2). The design included controls prepared with the steam sterilized soil treated with mercuric chloride. The $^{14}CO_2$ was captured in NaOH solution in an inner vial located within the sealed VOA vial. The NaOH solution was collected and analyzed for $^{14}CO_2$ concentrations by liquid scintillation counting. The rate of mineralization was determined by fitting the rate of $^{14}CO_2$ production to the Brunner and Focht three-half order rate equation.

The procedure for determining mineralization rates was as follows. A small (4 to 5-ml volume) vial containing 2 ml of 0.1 N NaOH was placed within the larger VOA vial atop the

Table 3-7

Chemical Analysis Required for the CNS Degradation Study

Test Type	Sample Type	Number of Sampling Periods Anticipated	Samples Per Sample Period	Total Number of Samples Anticipated	Sample Size	Parameter Measured	Method[1]
Component half-life	Soil	6 periods (At 2, 4, 8, 12, 16 weeks, and 6 months[2])	12	72	25 grams	Chloroform Chloropicrin Chloroacetophenone	GC (AP-0046)

(1) See Appendix B for details on methods and procedures.

(2) The experiment was discontinued at 6 weeks. Fewer sampling periods were required because the components dissipated early in the observation period.

soil, prepared in a similar fashion as in Section 3.2.4.2. One of the three components was added to the soil in each VOA vial. Each component addition included both radiolabeled (from Section 3.2.3) and unlabeled component. Sufficient neat component or spiking solution (neat component mixed with hexane) was added to bring the component concentration in soil to 100 mg/Kg. Typically, the component added to the soil consisted of approximately 99% unlabeled material with the remainder being ^{14}C-labeled component. The VOA vial was sealed and placed in a 25°C incubator. At the sampling times detailed in Table 3-6, treatment and control VOA vials were removed from the incubator, and the small, inner vial was removed and prepared for scintillation counting. At the sampling time, the VOA vials were placed in a freezer for 1 minute prior to opening. As VOA vials were opened, soil adhering to the outside of the small, inner vials was rinsed back into the respective VOA vials with 1 ml acetone. Immediately, 250 µl hexane was introduced into each small, inner vial, and the small, inner vial was capped. After several minutes, 100 µl of the hexane and 1 ml of the NaOH layer were placed in separate, prepared vials of scintillation cocktail and radioactivity measured as described in Appendix B. The soil in the respective VOA vials was sent to TVA's Specialty Laboratory and extracted. The CNS components were analyzed as described in Appendix B and reported in Section 3.2.4.2.

The hexane extract and the aqueous NaOH solution from each small, inner vial were prepared for scintillation counting. A scintillation cocktail was added to the hexane extract and the aqueous NaOH solution, and the mixtures were counted on a liquid scintillation counter. The scintillation cocktail is a mixture of chemicals which give off light when the mixture encounters radioactivity. By measuring the amount of light given off, it is possible to determine the amount of radiation being produced. The proportion of hexane extract and the aqueous NaOH sample to scintillation cocktail was adjusted so that either a clear liquid or a translucent gel was produced. If the hexane extract and the aqueous NaOH samples were found to photoluminesce, the samples were stored in the dark for a minimum of 24 hours to allow the photoluminescence to dissipate.

All samples measured by scintillation counting were corrected for quenching using a set of standards provided by Packard Instruments (Meriden, Connecticut) and compared to ^{14}C-labeled standards.

The cumulative production of $^{14}CO_2$ during degradation was fit to the three-half order equation of Brunner and Focht:

$$P = S_0\left(1 - e^{-k_1 t - (k_2 t^2)/2}\right) + k_0 t \qquad (10)$$

where P is product, the cumulative ^{14}C trapped, S_0 is the ^{14}C in initial substrate, k_1 is the first-order rate constant describing the initial mineralization of substrate, k_2 is a parameter describing linear increases in microbial degradative capacity, k_0 is the zero-order rate constant for mineralization of ^{14}C to transformed products, and t is the time interval after addition of ^{14}C.

3.2.5 Test Plan for the Soil Sorption Study

3.2.5.1 Overview

Soil sorption was determined by the batch equilibration method. An appropriate amount of air-dried contaminated soil from Area 15A and an aqueous solution containing a CNS component (either chloroform, chloropicrin, or phenacyl chloride) were mixed and equilibrated. After equilibration, the amount of CNS component in the solution was measured by GC. The amount of component sorbed on the soil was determined by difference between component applied and component remaining in solution (preliminary test) or component remaining in the soil (final test). The degree of soil sorption was expressed as the distribution coefficient. In the final test, five concentrations of the individual components, chloroform, chloropicrin, and phenacyl chloride, were examined. Details of the experimental design are shown in Table 3-8. Related analytical methods are provided in Table 3-9.

3.2.5.2 Determination of Soil Sorption Constants

The procedure for conducting the batch equilibration method was as follows. A preliminary test was conducted to determine the time period required for the concentration of an added

Table 3-8

Experimental Design of the Soil Sorption Study

Test Type	Type Sample	Sampling Times	CNS Component	Conc. Of Solution Added	Number of Replicates	Soil Required Per Replicate (grams)	Total Soil Required (grams)	Total Number of Samples
Preliminary Test	Contaminated Soil	2, 4, 8, 24 and 48 hrs	Chloroform	0.3 mM	1	5	25[1]	5[2]
			Chloropicrin	0.3 mM	1	5	25[1]	5[2]
			Phenacyl Chloride	0.03 mM	1	5	25[1]	5[2]
						Subtotal	75	15
Final Test	Contaminated Soil	1 Equilibration period	Chloroform	0, 20, 40, 60, 80 and 100 mg/L	3	5	90[3]	18[4]
			Chloropicrin	0, 20, 40, 60, 80 and 100 mg/L	3	5	90[2]	18[4]
			Phenacyl Chloride	0, 10, 20, 30, 40 and 50 mg/L	3	5	90[2]	18[4]
	Control (with no soil)	1 Equilibration period	Chloroform	0, 20, 40, 60, 80, and 100 mg/L	3	0	0	18[5]
			Chloropicrin	0, 20, 40, 60, 80, and 100 mg/L	3	0	0	18[5]
			Phenacyl Chloride	0, 10, 20, 30, 40, and 100 mg/L	3	0	0	18[5]
						Subtotal	270	108
						Totals	345	123

(1) Soil required = 5 equilibration times X 1 chemical concentration X 1 replicate X 5 grams per replicate = 25 grams.
(2) Sample number = 5 equilibration times X 1 chemical concentration X 1 replicate = 5 samples.
(3) Soil required = 1 equilibration time X 6 chemical concentrations X 3 replicates X 5 grams per replicate = 90 grams.
(4) Sample number = 1 equilibration time X 6 chemical concentrations X 3 replicates = 18 samples.

Table 3-9

Chemical Analysis Required for the Soil Sorption Study

Test	Sample Type	Number of Sampling Periods	Samples Per Sample Period	Total Number of Samples	Sample Size	Parameter Measured	Method [1]
Preliminary	Centrifuged Solution	5 periods (at 2, 4, 8, 24, and 48 hrs)	1	15	20 ml	Concentration of CNS Components	GC (AP-0046)
Final	Centrifuged Solution	1 period	108	108	20 ml	Concentration of CNS Components	GC (AP-0046)
Final	Soil	1 period	54	54	5 g	Concentration of CNS Components	GC (AP-0046)

(1) See Appendix B for details on methods and procedures.

component to reach an equilibrium in contaminated soil from Area 15A and an aqueous solution above the soil. Then a final test was conducted to determine the sorption constants for contaminated soil using the equilibration period determined in the preliminary test.

In the preliminary test, 5-g quantities of air-dried soil were combined with aqueous solutions of individual CNS components, 0.3 mM chloroform, 0.3 mM chloropicrin, and 0.03 mM phenacyl chloride in 25-ml Teflon™-capped, glass centrifuge tubes. Adequate tubes were prepared for three replicates of each soil-component mix. This allowed for harvest of the entire centrifuge tube contents at 2, 4, 8, 24, and 48 hours of incubation. After soil-component solution preparation, the tubes were placed on a shaker for the required incubation period. At the end of the appropriate incubation period, tubes were removed and centrifuged. The liquid above the soil was analyzed by GC for the corresponding component (Table 3-9). The amount of component sorbed to the soil was determined by the difference in solution concentration at the beginning and end of the test period time. The ratios of component sorbed to component initially introduced were plotted versus the incubation time to determine the time when a plateau, or equilibrium, was reached. The equilibration period was used in the final portion of the test.

For the final test, 5-g quantities of soil were mixed with 10-ml portions of component solutions at each of six concentrations of chloropicrin, chloroform, and phenacyl chloride. Three replicates of soil and the appropriate component at each concentration level were prepared. The component concentration ranges were 0, 20, 40, 60, 80 and 100 mg/L chloroform and chloropicrin and 0, 10, 20, 30, 40, and 50 mg/L phenacyl chloride in aqueous 0.01 M $CaCl_2$ solution. A set of control tubes containing the same volume and concentration of each component solution, but not containing soil, was also included. The controls were used for a materials balance to evaluate the loss of components during incubation to such factors as volatilization. All samples and controls were treated identically.

Stock solutions of 1,000 mg/L chloroform, 1,000 mg/L chloropicrin, and 500 mg/L phenacyl chloride in 0.01 M $CaCl_2$ were prepared several days prior to initiating sorption experiments. On the day before the start of incubation, each 5-g quantity of soil received the appropriate amount of aqueous 0.01 M $CaCl_2$ solution, a minimum of 9 ml, for diluting the stock to appropriate concentration. The soil was allowed to equilibrate with the aqueous 0.01 M $CaCl_2$

solution overnight with shaking at 275 rpm on a Thermolyne Sybron LE Rotator/Shaker (Barnstead/Thermolyne, Dubuque, Iowa). At the beginning of incubation, an appropriate amount of stock solution of the appropriate component was added to each tube of soil to result in the desired soil-component solution concentration. The actual ratio of air-dried soil to volume of solution was determined from the characteristics of the soil and the components in question.[Ref. 16] The 1 to 4 soil to solution ratio used for the preliminary trial was theoretically adequate to allow adsorption of 20% or more of the individual components to soil, a change in component concentration readily detectable by GC analysis (Table 3-9). Similarly, a ratio of 1 to 2 soil to solution was used for the final trial. The 0.01 M $CaCl_2$ aqueous solution eliminated ionic strength effects. The tubes were shaken at 275 rpm for 48 hours. At the end of the equilibration period, the tubes were centrifuged for 3 minutes. An aliquot of solution above the soil was removed for GC analysis. The residual soil was extracted with hexane, and GC analysis was conducted (Table 3-9). The log of the concentration of components in the solution above the soil and the log of the concentration of the components sorbed to the corresponding soil were graphed as Freundlich isotherms for prediction of K_D.

Soil sorption was reported as the distribution coefficient (K_D) which indicates the degree of sorption. The distribution coefficient is calculated as:

$$K_D = S / C \qquad (11)$$

where S is the amount of component sorbed to soil at the end of equilibration and C is the amount of component in solution at the end of equilibration. K_D is a widely reported parameter frequently required for mathematical simulations.

3.2.6 Test Plan for the Volatility Study

3.2.6.1 Overview

Both the vapor densities and Henry's Law Coefficients were either obtained directly from literature or calculated on the basis of additional physical characteristics reported in the scientific literature.

3.2.6.2 Determination of Vapor Density

When the vapor density of a CNS component was not directly available from the literature, the component's vapor density was calculated from currently available literature values for vapor pressure using Equation 12 below.

$$d = 0.12\left(\frac{pM}{T}\right) \tag{12}$$

where d is the vapor density in µg/L, p is the vapor pressure in mPa, M is the molecular weight of the component, and T is the absolute temperature in °K. Vapor pressure data were available for all components.

3.2.6.3 Determination of Henry's Law Coefficients

Henry's Law Coefficients (h) were calculated for CNS components using the vapor density of the saturated vapors (d_0) from Equation 12 above and concentrations of saturated solutions (c_0) obtained from the literature according to Equation 13 below.

$$h = \frac{d_0}{c_0} \tag{13}$$

3.2.7 Test Plan for the Transport Study

3.2.7.1 Overview

The soil-gas diffusion coefficients of CNS components were calculated using literature sources for the input variables to the equations listed below.

3.2.7.2 Determination of Soil-Gas Diffusion Coefficients

Soil-gas diffusion for the contaminated soil was characterized with the soil-gas diffusion coefficient, D_G, as determined from the Millington-Quirk model.[Ref. 17] In this model, D_G is dependent on the air-gas diffusion coefficient, D_G^{air}, and a tortuosity factor that accounts for reduced flow and increased path length in soil.

$$D_G = \left(\frac{a^{10/3}}{\phi^2} \right) D_G^{air} \qquad (14)$$

where ϕ is the soil porosity and a is the volumetric air content.

The air-gas diffusion coefficient was estimated from literature data.[Refs. 7,18,&19] Previous research has shown that representative values for similar chemicals were adequate and did not need to be measured in every case.[Ref. 19] Values for both ϕ and a were developed from the particle size distribution data from the soil characterization study. The soil porosity (ϕ), expressed as a percent, was calculated from the equation:

$$\phi = (1 - \frac{\rho_b}{\rho_p}) * 100 \qquad (15)$$

where the bulk density (ρ_b) of the contaminated soil was determined by drying a specific volume of a core sample to constant weight at 105°C. The particle density (ρ_p) was determined by the pycnometer method (Appendix B-6). The soil moisture was determined as the ratio of mass of water to the dry mass and reported as a percentage.

3.2.7.3 Determination of the Kinematic Viscosity of Chloropicrin

The kinematic viscosity of chloropicrin was measured in accordance with ASTM Method D 445-94, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)" (Appendix B-7). The device used was a Cannon Ubbeholde Size 25 viscometer with a calibration factor of 0.000179 centistokes/second. The viscometer was placed in a large, stirred-water bath and charged with chloropicrin. The flow times for chloropicrin over the range of 0°C to 30°C were measured. Temperature was measured with a calibrated thermometer, traceable to the National Institutes of Standards and Technology. The thermometer was calibrated by Ever Ready Thermometer Company of New York, New York. The resulting data yielded values for kinematic viscosity in centistokes versus temperature. These values were then converted to a polynomial equation using curve fitting techniques.

3.2.7.4 Determination of the Viscosity of Chloropicrin

The viscosity of chloropicrin was determined by multiplying the polynomial equation for kinematic viscosity by the polynomial equation for the density of chloropicrin at the same temperature interval. The kinematic viscosity of chloropicrin was obtained from the polynomial equation developed in Section 3.2.7.3 above. The density of chloropicrin was obtained by directly measuring the density in the laboratory and then converting these measurements to a polynomial equation.

The density of chloropicrin was obtained by placing 5 ml of chloropicrin (8.2799 g) into a 10-ml graduated cylinder, sealing the graduated cylinder with two layers of Parafin "M" laboratory film, placing the cylinder in a thermostatted recirculating bath, allowing the cylinder to equilibrate, and measuring the volume of the liquid within the cylinder at 5-degree intervals from 0°C to 30°C. The cylinder was allowed to equilibrate for at least 3 minutes between each measurement.

Calibration of the cylinder had been verified by weighing distilled water at the 4, 5, 6, and 7 ml marks. All weighings were done on an analytical balance that had been recently calibrated by

TVA's balance calibration service which is traceable to NIST. Calibration of the balance was checked before use with a standard weight.

3.3 Sample Labeling

All samples were labeled with an identification code identifying the treatment, type of test, component, soil, replicate number, date, and person sampling. A few examples are shown in Table 3-10. The first set of identifiers represents the treatment, type of test, component, and replicate number. The treatment, component concentration in this case, was represented by a sequential number. The next character was the type of test represented by S for sorption, D for degradation. Components were represented by F for chloroform, P for chloropicrin, A for chloroacetophenone, and N for none. The final number in the first set of identifiers represents the replicate number. The next identifier represents the soil sample, in this case identified as Soil or None for no soil. The third identifier was the date the sample was taken. The fourth and final identifier was the initials of the person sampling.

For example, the first identification number for the soil sorption study was 3SF1.None.11/1/96.SSH which stands for CNS component concentration three (3), soil sorption study (S), chloroform (F), replicate number 1, with no soil, sampled on 11/1/96, by Sidney Harper.

3.4 Laboratory Equipment

Equipment used for laboratory data collection is outlined in Table 3-11. All procedures are referenced in Appendix B.

3.5 Chain of Custody

Soil samples transported to the ERC were subject to chain-of-custody procedures (see sampling plan in Appendix A). Samples being moved between departments within the ERC were appropriately labeled but were not subjected to further chain-of-custody procedures due to the departments' close proximity and location in a single building (the ERC building).

Table 3-10

Sample Identification for Collected Samples

Sorption	Degradation
3SF1.None.11/1/96.SSH	1DN1.Soil1.11/1/96.SSH
3SF2.None.11/1/96.SSH	1DN2.Soil1.11/1/96.SSH
3SF3.None.11/1/96.SSH	1DN3.Soil1.11/1/96.SSH
0SF1.Soil1.11/1/96.SSH	1DF1.Soil1.11/1/96.SSH
0SF2.Soil1.11/1/96.SSH	1DF2.Soil1.11/1/96.SSH
0SF3.Soil1.11/1/96.SSH	1DF3.Soil1.11/1/96.SSH
1SF1.Soil1.11/1/96.SSH	1DP1.Soil1.11/1/96.SSH
1SF2.Soil1.11/1/96.SSH	1DP2.Soil1.11/1/96.SSH
1SF3.Soil1.11/1/96.SSH	1DP3.Soil1.11/1/96.SSH
2SF1.Soil1.11/1/96.SSH	1DA1.Soil1.11/1/96.SSH
2SF2.Soil1.11/1/96.SSH	1DA2.Soil1.11/1/96.SSH
2SF3.Soil1.11/1/96.SSH	1DA3.Soil1.11/1/96.SSH
3SF1.Soil1.11/1/96.SSH	1DN1.Soil2.11/1/96.SSH
3SF2.Soil1.11/1/96.SSH	1DN2.Soil2.11/1/96.SSH
3SF3.Soil1.11/1/96.SSH	1DN3.Soil2.11/1/96.SSH
4SF1.Soil1.11/1/96.SSH	1DF1.Soil2.11/1/96.SSH
4SF2.Soil1.11/1/96.SSH	1DF2.Soil2.11/1/96.SSH
4SF3.Soil1.11/1/96.SSH	1DF3.Soil2.11/1/96.SSH
5SF1.Soil1.11/1/96.SSH	1DP1.Soil2.11/1/96.SSH
5SF2.Soil1.11/1/96.SSH	1DP2.Soil2.11/1/96.SSH
5SF3.Soil1.11/1/96.SSH	1DP3.Soil2.11/1/96.SSH
	1DA1.Soil2.11/1/96.SSH
	1DA2.Soil2.11/1/96.SSH
	1DA3.Soil2.11/1/96.SSH

Table 3-11

Equipment Used for Data Collection

Laboratory Data	Equipment
^{14}C	Packard Liquid Scintillation Counter
pH	Orion Meter
Chemical Synthesis of Chloroform, Chloropicrin, and Phenacyl Chloride	Varian GC
Viscosity	Cannon Ubbeholde Size 25 viscometer

SECTION 4.0
STUDY RESULTS

4.1 Results of the Soil Characterization Study

4.1.1 Concentration of CNS Components in Soil

The CNS component concentrations from contaminated soil at Area 15A varied from 23.4 to 31.4 mg/Kg (Table 4-1). The soils sampled were obtained at depths between 6 to 9.5 feet below the surface.

4.1.2 pH of Soil

The pH of the soil from the Area 15A and surrounding areas was acidic and varied from a pH of 3.89 to a pH of 5.72 (Table 4-2). These determinations were performed in triplicate, and the mean values are reported.

4.1.3 Organic Carbon Content of Soil

The organic carbon content of the uncontaminated soil from the area surrounding Area 15A was generally low and varied from 0.18 to 3.85% by weight (Table 4-2). The contaminated soil from Area 15A had an organic carbon content of 0.48% by weight. These determinations were performed in triplicate, and the mean values are reported.

4.1.4 Moisture Content of Soil

The average moisture content of the contaminated soil obtained from Area 15A at a depth of 6 to 9.5 feet was 11.6% by weight.

Table 4-1

Concentrations of CNS Components in Contaminated Soil from Area 15A

	Component Concentration		
Soil Depth (feet)	**Chloroform (mg/Kg)**	**Chloropicrin (mg/Kg)**	**Chloroacetophenone (mg/Kg)**
6 to 9.5	25.8	23.4	31.4

Table 4-2

pH and Organic Carbon Content of Soils

Soil Source	Soil Depth	Soil Type	pH[1]	Organic Carbon[1] (%)
Area 1	6" to 2'	Non-Contaminated	5.72	0.62
	2' to 4'	Non-Contaminated	5.01	0.23
Area 2	6" to 2'	Non-Contaminated	4.94	0.34
	2' to 4'	Non-Contaminated	4.96	0.22
	4' to 6'	Non-Contaminated	4.78	0.18
Area 3	0' to 3'	Non-Contaminated	4.94	0.74
	3' to 6'	Non-Contaminated	5.38	0.62
Area 4	6' to 8'	Non-Contaminated	5.27	3.85
Area 15A	6' to 9.5'	Contaminated	3.89	0.48

1) Average of triplicate analysis.

4.1.5 Particle Size Distribution of Soil

The sand, silt, and clay soil particle size distribution of the uncontaminated soil was analyzed by the sieve method (ASA Method 15-5, Appendix B-3). The soil constituents were characterized on the basis of respective particle diameters according to the following criteria:

- Sand, between 50-2000 μm (by weight)
- Silt, between 2-50 μm
- Clay, less than 2 μm

The test results for the uncontaminated soil indicate the particle size distribution of the uncontaminated soil was as follows:

- Sand, 11.8% to 56.6% (by weight)
- Silt, 24.5% to 61.0%
- Clay, 18.9% to 30.8%

The texture of these soils included loam, silt/loam, sandy/loam, and silty/clay/loam. A more detailed listing of the particle size distribution results with uncontaminated soil is provided in Table 4-3.)

Both sieve and hydrometer methods (ASTM D422, Appendix B-6) were utilized to characterize the contaminated soil; consequently, the particle size distribution of contaminated soil from Area 15A was determined to a fuller extent than that for the uncontaminated soil. With respect to particle size, 100% of the contaminated soil passed through a No. 10 (2 mm) sieve. The percentage of soil passing through successive sieve sizes was as follows:

- 74 μm, 83.2% passed through (by weight)
- 50 μm, 77.8% passed through
- 5 μm, 45.2% passed through
- 2 μm, 32.3% passed through

Table 4-3

Particle Size Distribution of Uncontaminated Soils as Determined by the Hydrometer Method

Soil Source	Soil Depth	Soil Texture	Sand (%)	Silt (%)	Clay (%)	Time (min)	Particle Diameter (μm)	Soil in Suspension (%)
Area 1	6" to 2'	silt loam	18.2	57.7	24.1	0.5	60.5	84.3
						1	43.3	79.8
						90	5.1	33.5
						1,440	1.3	19.9
	2' to 4'	loam	33.6	39.4	27.0	0.5	62.2	69.8
						1	44.7	64.7
						90	5.1	35.7
						1,440	1.3	23.0
Area 2	6" to 2'	loam	48.3	34.0	17.7	0.5	64.7	55.6
						1	46.4	50.6
						90	5.2	27.8
						1,440	1.3	13.5
	2' to 4'	loam	43.6	34.1	22.0	0.5	64.2	59.2
						1	45.9	54.9
						90	5.1	30.9
						1,440	1.3	18.0
	4' to 6'	sandy loam	56.6	24.5	18.9	0.5	66.1	47.6
						1	47.4	42.5
						90	5.2	27.2
						1,440	1.3	15.3
Area 3	0' to 3'	silty clay loam	14.1	56.2	29.7	0.5	59.6	87.3
						1	42.5	84.6
						90	5.0	42.3
						1,440	1.3	23.8
	3' to 6'	silty clay loam	8.2	61.0	30.8	0.5	57.6	95.6
						1	41.8	87.8
						90	5.0	44.8
						1,440	1.3	24.1
	6' to 8'	silty clay loam	11.8	59.1	29.1	0.5	59.1	91.2
						1	42.3	86.8
						90	5.0	48.7
						1,440	1.3	21.3

A chart showing the percent of contaminated soil in suspension as a function of particle size is shown in Figure 4-1. The particle size distribution of the contaminated soil was as follows:

- Sand, 21.4% to 22.3% (by weight)
- Silt, 46.8% to 45.5%
- Clay, 31.8% to 32.3%

A comparison of the particle size distribution developed by both the sieve and hydrometer methods showed the results were in good agreement (Table 4-4). The contaminated soil had a silt/loam/clay texture with a specific gravity (i.e., particle density) of 2.65 g/cm^3.

4.2 Synthesis of Labeled Compounds

4.2.1 Synthesis of Chloropicrin-^{14}C

Chloropicrin-^{14}C was prepared as described in Section 3.2.3.2. The product recovered represented 13.5% of the theoretical yield of chloropicrin (0.07 mmole) and a calculated radioactivity of 67.7 μCi. A scintillation count of the product showed actual radioactivity of 62.9 μCi, indicating that the preponderance of label in the product was chloropicrin-^{14}C.

4.2.2 Synthesis of Phenacyl Chloride-Ring-UL-^{14}C

Uniformly labeled phenacyl chloride (phenacyl chloride-ring-UL-^{14}C) was prepared as described in Section 3.2.3.3. The product was recovered in acetone. An additional benzene rinse was made of the distillation flask. The combined acetone and benzene extracted phenacyl chloride (0.03 mmole) represents 5.3% of the theoretical yield of phenacyl chloride and a calculated radioactivity of 26 μCi. A scintillation count of the product showed actual radioactivity of 27.8 μCi, indicating that the preponderance of label in the product was phenacyl chloride-ring-UL-^{14}C.

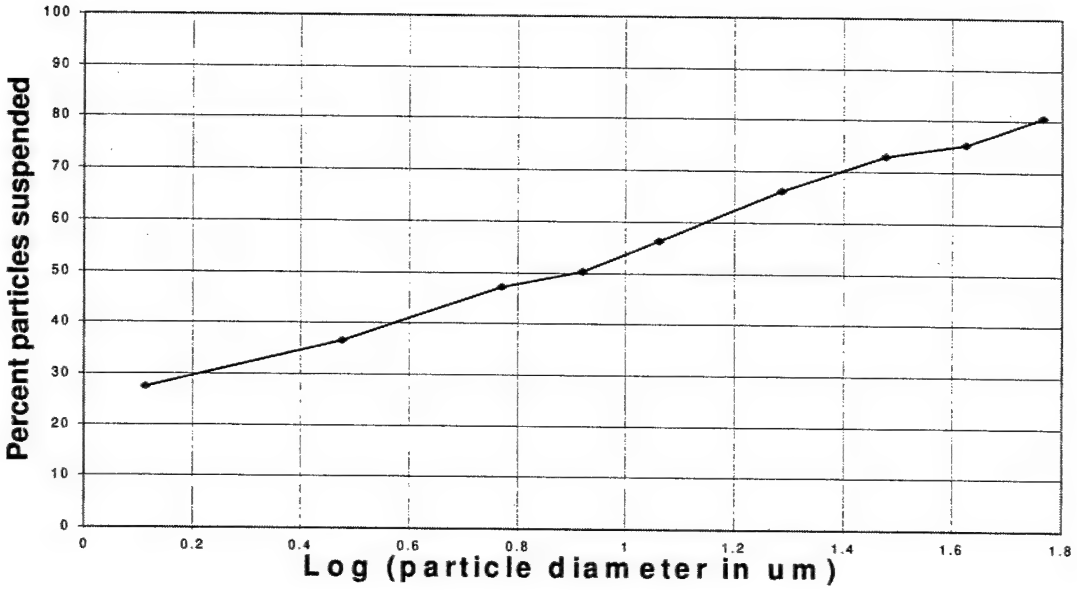


Figure 4-1

Percentage of Contaminated Soil in Suspension as a Function of Particle Size

Table 4-4

Comparison Particle Distribution of Contaminated Soil from Area 15A by Two Characterization Methods[1]

	Hydrometer Method	Sieve Method	Soil Texture
Percentage Clay	31.8%	32.3%	Silty clay loam
Percentage Silt	46.8%	45.5%	
Percentage Sand	21.4%	22.3%	

(1) Soil obtained from a depth of 6 to 9.5 feet.

4.2.3 Synthesis of Phenacyl Chloride-Carbonyl-^{14}C

Uniformly labeled phenacyl chloride (phenacyl chloride-carbonyl-^{14}C) was prepared as described in Section 3.2.3.3. The product was recovered with a benzene rinse. The phenacyl chloride recovered (0.07 mmole) represents 14% of the theoretical yield of phenacyl chloride and a calculated radioactivity of 69.5 μCi. A scintillation count of the product showed actual radioactivity of 86.8 μCi, indicating a likely preponderance of phenacyl chloride-carbonyl-^{14}C but presence of extraneous label in an unidentified form.

4.3 Results of the CNS Degradation Study

4.3.1 Component Half-Life

The component half-life, $T_{1/2}$, was determined by the relationship

$$T_{1/2} = \frac{-0.693t}{\ln\left(\frac{M_t}{M_0}\right)}$$

where M_0, is the amount of chloroform, chloropicrin, or phenacyl chloride in the soil at the outset of incubation and M_t is the amount remaining in the soil at time interval, t.

Linear regressions were calculated assuming a starting concentration of 100 mg component per g soil and using 14- and 35-day data in the cases of chloroform and chloropicrin and 14-, 35- and 42-day data in the case of phenacyl chloride. Respective $T_{1/2}$ values are 6, 6, and 36 days for chloroform, chloropicrin, and phenacyl chloride (Table 4-5). Degradation is assumed to follow first order kinetics.

As additional confirmation of these results, the components remaining in soil over the course of the mineralization rate determination (Section 4.4) were analyzed by GC. The persistence of the compounds was evaluated, and half-lives of 2, 6, and 36 days were calculated where labeled components had been added.

Table 4-5

CNS Component Half-Life - Based on Persistence of Components in Soil During the Component Half-Life Test

CNS Component	Component Concentration Remaining in Soil[1] (mg/Kg)				Component Half-life (days)
	0 hour	2 weeks	5 weeks	6 weeks	
Chloroform	100	44.3	1.6	0	6
Chloropicrin	100	55.1	1.4	0	6
Phenacyl Chloride	100	77.7	49.7	45.3	36

(1) Average of four determinations.

After incubation, the control vials contained nearly identical amounts of chloroform, chloropicrin, and phenacyl chloride. This indicates that the rate at which the CNS components disappeared from within the control vials was as rapid as that found in the treatment vials. For this reason, the control vial data were included as a fourth replicate in Table 4-5. In theory, loss of the CNS components from the control vials should reflect abiotic (nonbiological) activity, while loss of these components in the treatment vials should reflect a combination of biotic (biological) and abiotic activity. The control vials contained sterilized soil and were processed along side the treatment vials containing soil that had not been sterilized. Therefore, it is unclear why the rates of component loss in the control and treatment vials were so similar; possible explanations include:

1) The control soil may not have been sterile either due to the inherent difficulty in sterilizing soil or due to the reintroduction of microbes.

2) The rate of component disappearance due to abiotic factors may exceed the rate of disappearance due to biotic factors. The abiotic factors involved could include: volatilization or soil sorption or surface chemical degradation.

The sorption studies (Section 4.4) showed that adsorption is not a significant route of component removal in the soil. The best explanation may be that the soil was actually not sterile. Although no test was made to determine the sterility of the control soil, a subsequent test identified a microbial population, although relatively small, in the stored CNS contaminated soil.

4.3.2 Mineralization Rates

In this experiment, the mineralization rates for each CNS component were determined by measuring the amount of ^{14}C-labeled carbon dioxide gas ($^{14}CO_2$) produced during mineralization. The experiments were designed similarly to those used to determine the half-life (Section 3.2.4.2). The design included controls prepared with the steam sterilized soil which had been treated with mercuric chloride to further assure sterilization. The $^{14}CO_2$ was captured in NaOH solution in an inner vial located within a sealed VOA vial. The NaOH solution was subsequently collected, extracted with hexane to remove any CNS components present, and analyzed for $^{14}CO_2$ by liquid scintillation counting. The rate of mineralization was

determined by fitting the rate of $^{14}CO_2$ production to the Brunner and Focht three-half order rate equation (see Section 3.2.4.3). This model assumed that the CNS components were subject to one of three fates:

1) Mineralization to $^{14}CO_2$
2) Incorporation into the soil humus
3) Incorporation into biomass

According to this model, any ^{14}C present in the extracted NaOH solution is assumed to be radiolabeled CO_2 present, as a result of the mineralization of the radiolabeled component. In this model, the rate of mineralization is calculated on the basis of the amount of mineralizable ^{14}C present in the soil as opposed to the amount of ^{14}C originally present in the soil. The amount of ^{14}C available for mineralization is assumed to equal the difference between the amount of ^{14}C originally introduced into the soil and the amount of ^{14}C in the humus. The amount of ^{14}C present in the biomass is either ignored, included in the humus count, or accounted for in the sterilized control. The model assumes that incorporation of the ^{14}C in humus occurs at the outset of incubation (at 0 hour). Therefore, the amount of ^{14}C present in the humus is determined by extrapolating a linear plot of the amount of ^{14}C in the extracted NaOH solution versus time to time equals zero. At time equals zero, the 0 hour, the amount of ^{14}C registering on the plot's y-axis is assumed to be the amount of ^{14}C in the humus.

The amount of ^{14}C originally present in the soil was determined by a scintillation count of the stock solution of each labeled component. Extrapolation of a linear plot of product versus time indicated that the percent of ^{14}C incorporated into humus for each component was:

- Chloroform, 10.5% of the amount of ^{14}C introduced
- Chloropicrin, -24.7% of the amount of ^{14}C introduced
- Phenacyl chloride, -1% of the amount of ^{14}C introduced

Therefore, the percent of mineralizable ^{14}C available for degradation for each component was:

- Chloroform, 89.5% of the amount of ^{14}C introduced
- Chloropicrin, 124.7% of the amount of ^{14}C introduced
- Phenacyl chloride, 101.0% of the amount of ^{14}C introduced

Incorporation of this mineralizable ^{14}C into product $^{14}CO_2$ followed first-order rate kinetics at the following rates for each component:

- Chloroform, -0.0025 day^{-1}
- Chloropicrin, -3.33 day^{-1}
- Phenacyl chloride, -0.11 day^{-1}

These rates were used then used to calculate a mineralization half-life for each component (Table 4-6). These mineralization half-lives were:

- Chloroform, 227.2 days
- Chloropicrin, 0.21 days
- Phenacyl chloride, 6.3 days

A comparison of the component half-lives of chloropicrin and phenacyl chloride in soil, 6 and 36 days, respectively (Table 4-5), were comparable to their mineralization half-lives, 0.21 and 6.3 days, respectively (Table 4-6). However, the component half-life of chloroform in soil (5.3 days) was substantially less than chloroform's mineralization half-life (227.2 days), indicating that chloroform degrades much faster than it is mineralized. This may reflect a relatively rapid degradation of chloroform to intermediates which are slowly released as CO_2 or binding of chloroform to soil in a form which cannot be readily extracted.

Table 4-6

Component Mineralization Rates and Half-Life - Based on Persistence of ^{14}C in Soil During the Mineralization Test

Chemical Component	% of ^{14}C in Soil which is "Mineralizable"	% of ^{14}C in Soil which has been Incorporated in the Humus	Fraction of the "Mineralizable" ^{14}C Substrate Remaining in Soil Over Time				Rate of Mineralization ($Days^{-1}$)	Mineralization Half-Life (Days)
			0 hour	2 weeks	5 weeks	6 weeks		
Chloroform	89.5	10.5	0	0.031	0.071	0.094	-0.0025	227.2
Chloropicrin	124.7	-24.7	0	0.558	1.258	1.673	-3.33	0.2
Phenacyl Chloride	101.0	-1	0	0.018	0.044	0.065	-0.11	6.3

(1) Summary of replicate determinations.

As an additional confirmation of the results, the CNS components remaining in soil over the mineralization rate test were extracted and analyzed by GC (Table 4-7). Linear regressions of the data resulted in calculated component half-lives of:

- Chloroform, 2 days
- Chloropicrin, 6 days
- Phenacyl chloride, 36 days

This data compares favorably with the component half-lives of 6, 6, and 36 days for chloroform, chloropicrin, and phenacyl chloride, respectfully, reported in Section 4.3 (Table 4-5).

As in the test to determine component half-lives in soil (see Section 4.3), no differences in the rates of mineralization/degradation were seen between control and treatment vials incubated for the same period of time. This occurred even though the soil in the control VOA vials had been sterilized by steam sterilization and addition of mercuric chloride during both tests. Similar amounts of $^{14}CO_2$ were found in the hexane extracts and aqueous NaOH solutions obtained from the inner vials of the larger control and treatment VOA vials. Likewise, similar amounts of residual chloroform, chloropicrin, and phenacyl chloride were found in the soil within the control and treatment VOA vials. This indicates that the sterilized soil likely had a reinitiation of microbial activity during both tests or the level of microbial activity was low in all cases and the observed degradation was influenced by other factors. The mineralization test was discontinued after 6 weeks because no chloroform or chloropicrin remained in the soil after this period.

4.4 Results of the Soil Sorption Study

Soil sorption was determined by the batch equilibration method (see Section 3.2.5). During this test, an appropriate amount of air-dried soil and an aqueous solution containing a CNS component (either chloroform, chloropicrin, or phenacyl chloride) was mixed and equilibrated. After equilibration, the amount of CNS component in the solution was measured by GC. The amount of component sorbed on the soil was determined by difference between component

Table 4-7

Component Half-Life - Based on Persistence of Component in Soil During the Mineralization Test

CNS Component	Component Concentration Remaining in Soil[1] (mg/Kg)				Component Half-Life (days)
	0 hour	2 weeks	5 weeks	6 weeks	
Chloroform	100	1.3	0	0	2
Chloropicrin	100	13.6	0	0	6
Phenacyl Chloride	100	59.4	47.4	42.1	36

(1) Summary of replicate determinations.

applied and component remaining in solution (preliminary test) or component remaining in the soil (final test). The preliminary test was conducted to determine the time period required for the concentration of an added component to reach an equilibrium in soil and the aqueous solution above the soil. The final test was conducted to determine the sorption constants using the equilibration period determined in the preliminary test.

The data generated during this test were used to plot Freundlich isotherms for prediction of distribution coefficient (K_d) (Table 4-8). The linear form of the Freundlich adsorption equation is expressed as:

$$\log C_{soil} = \log K_F + \frac{1}{n} * \log C_{solution}$$

where C_{soil} is the component concentration adsorbed to soil, $C_{solution}$ is the component concentration in the solution above the soil, n is a constant, and K_F is the Freundlich adsorption coefficient. The Freundlich adsorption coefficient is equal to the K_d when the regression constant 1/n is close to 1.0. The data obtained during this test resulted in good fits and 1/n values approaching 1.0 for the linearized plot of each component. Based on these results the K_d values for each component were as follows (see also Table 4-8):

- Chloroform, 1.84
- Chloropicrin, 1.87
- Phenacyl chloride, 3.43

For comparison purposes, the K_d was also estimated from several physical characteristics of organic chemicals. Theory states that the K_d is directly related to the amount of organic matter in the soil. Consequently, some researchers have tested a variety of soils with varying amounts of organic matter and published organic carbon normalized adsorption coefficients (K_{OC}). The relationship of K_{OC} to K_d is expressed as:

$$K_{OC} = K_d * \frac{100}{\%OC}$$

Table 4-8

Soil Sorption Test - Determination of K_d for Contaminated Soil

Chemical Component	Initial Concentration of Component (mg/L)	Concentration of Component Sorbed to Soil (mg/Kg)	Concentration of Component is Liquid Above Soil (mg/L)	K_d From Freundlich Adsorption Isotherm
Chloroform	0	0.12	0.23	1.84
	20	10.77	19.40	
	40	20.31	36.57	
	60	32.00	55.96	
	80	39.26	65.06	
	100	51.28	79.62	
Chloropicrin	0	0.12	0.25	1.87
	20	13.73	23.87	
	40	23.37	41.76	
	60	37.41	62.79	
	80	45.12	72.30	
	100	57.90	95.18	
Phenacyl Chloride	0	0.32	1.30	3.43
	10	3.39	10.10	
	20	7.20	18.31	
	30	11.50	27.26	
	40	15.73	34.14	
	50	20.58	43.31	

K_{OC} has also been related by the octanol-water coefficient (K_{OW}) and to water solubility by a number of researchers. There are various equations for the relationships.

In theory, sorption is directly influenced by soil organic matter. The organic fraction of the contaminated soil was relatively small, 0.48 g C per 100 g soil (see Section 4.1.3 and Table 4-2). However, with charged materials, pH can influence sorption. In the CNS component tests, the pH of the soil and component solution are expected to have little impact on sorption. Nevertheless, the pH of the soil and soil solution were documented. The pH of soil prior to addition of 0.01 M $CaCl_2$ was 3.86 and 4.12 after 48 hours in the presence of 0.01 M $CaCl_2$.

Using the tear gas-contaminated soil organic carbon composition of 0.48% and published physical characteristics, calculated K_d values were developed and compared to the values obtained during the test (Table 4-9). The K_d values for chloroform and chloropicrin obtained by experimentation show somewhat more of a tendency for sorption than the calculated values indicate. However, the general trends indicate sorption is not a major factor in degradation dynamics for chloroform and chloropicrin. The experimental K_d for phenacyl chloride lies within the range of the two calculated values. Sorption is of more significance in the degradation dynamics of phenacyl chloride.

4.5 Results of the Volatility Study

4.5.1 Vapor Density

The vapor pressures of the CNS components are provided in Table 4-10. These values were calculated from vapor pressure data by the method described in Section 3.2.6.2.

4.5.2 Henry's Law Coefficients

The Henry's Law Coefficients for each CNS component are provided in Table 4-11. The Henry's Law Coefficient for each CNS component was calculated using the vapor density of saturated vapors and the concentration of saturated solutions as described in Section 3.2.6.3.

Table 4-9

Soil Sorption Test - Comparison of Calculated K_d Values to the Experimentally Determined Values

CNS Component	K_d Calculated Using Published Fate and Transport Characteristic		Experimentally -Determined K_d
	Published Characteristic	Calculated K_d	
Chloroform	$\log K_{OC} = 44$ [Ref. 20]	0.21	1.84
	Solubility = 8.2 g/L [See Table 5-1]	0.16	
	$\log K_{OW} = 1.97$ [Ref. 21]	0.55	
Chloropicrin	$\log K_{OW} = 2.09$ [Ref. 20]	0.72	1.87
	$K_{OC} = 200$ [Ref. 22]	0.96	
	Solubility = 1.5 g/L [See Table 5-1]	0.46	
Phenacyl Chloride	$K_{OC} = <912$ [Ref. 22]	<4.38	3.43
	Solubility = >0.5 g/L [1] (See Table 5-1)	>0.90	

(1) Conclusion reached due to inability to dissolve 1 g phenacyl chloride in a liter of 0.01 M $CaCl_2$, but ability to dissolve 0.5 g in 1 liter

Table 4-10

Volatility Study - Vapor Densities of CNS Components

CNS Component	Vapor Pressure (kPa @ 20°C)	Vapor Density[1] (g/L)
Chloroform	21.5	1.05
Chloropicrin	2.26	0.15
Phenacyl Chloride	7.2×10^{-4}	4.56×10^{-5}

(1) Vapor densities were calculated from vapor pressures as described in Section 3.2.6.2.

Table 4-11

Volatility Study - Henry's Law Coefficients of CNS Components[1]

CNS Component	Henry's Law Coefficient
Chloroform	0.13
Chloropicrin	0.10
Phenacyl Chloride[2]	9.12×10^{-5} to 4.56×10^{-5}

(1) Calculated from vapor density of saturated solutions.

(2) The solubility of phenacyl chloride in water was found to be between 0.5 and 1.0 g/L.

4.6 Results of the Transport Study

4.6.1 Soil-Gas Diffusion Coefficient

The soil-gas diffusion coefficient was calculated from the equation:

$$D_G = \frac{a^{\frac{10}{3}}}{\phi^2} * D_G^{air}$$

where D_g^{air}, the gas diffusivity, is 0.43 m^2 air d, $\emptyset$ is the soil porosity, and a is the soil air content. The soil porosity (ϕ), expressed as a percent, was calculated from the equation:

$$\phi = (1 - \frac{\rho_b}{\rho_p}) * 100$$

where ρ_b is the bulk density of the contaminated soil and ρ_p is the particle density of the contaminated soil. The bulk density (ρ_b) of the contaminated soil was determined by drying a specific volume of a core sample to constant weight at 105°C to determine the moisture content of the soil. The particle density (ρ_p) was determined by pycnometer methods (see Section 3.2.7).

The results indicated that the soil-gas diffusion coefficient for the contaminated soil from Area 15A at a depth of 6 to 9.5 feet was 1.8 m^2/day (Table 4-12).

4.6.2 Kinematic Viscosity of Chloropicrin

The kinematic viscosity of chloropicrin was measured between the temperatures of 0°C to 29.4°C using a viscometer (Table 4-13). The estimated uncertainty within a single measurement was on the order of one second with repeatability of measurements with deionized water on the order of five to seven seconds. All flow times for these measurements were greater than the 200 second minimum recommended by ASTM.

Table 4-12

Transport Study - Soil-Gas Diffusion Coefficient of Contaminated Soil and Related Information (Soil Moisture Content, Bulk Density, Particle Density, and Soil Porosity)

Soil Source	Soil Depth (feet)	Moisture (%)	Bulk Density (g/cm^3)	Particle Density (g/cm^3)	Soil Porosity (%)	Soil-Gas Diffusion (m^2/day)
Area 15A	6 to 9.5	11.6	1.67	2.56	34.8	1.8

Table 4-13

Determination of the Viscosity of Chloropicrin - Flow Time, Temperature, and Kinematic Viscosity Data from Laboratory Testing

Temperature (°C)	Total Time (Seconds)	Kinematic Viscosity (Centistokes)
0.0	456.5	0.8171
0.5	455.94	0.8161
2.9	439.4	0.7865
3.6	435.1	0.7788
4.9	426.8	0.7640
6	419.24	0.7504
7.2	412.36	0.7381
8.3	405.58	0.7260
10.5	392	0.7017
11.0	390.39	0.6988
11.5	388.13	0.6948
13.0	379.48	0.6793
13.5	378.06	0.6767
15.0	370.47	0.6631
15.2	369.2	0.6609
16.0	363.47	0.6506
16.4	362.31	0.6485
17.0	359.27	0.6431
17.6	356.51	0.6382
20.3	344.97	0.6175
20.3	344.53	0.6167
20.5	343.4	0.6147
22.8	333.63	0.5972
22.9	332.64	0.5954
23.0	332.17	0.5946
24.1	327.3	0.5859
24.3	327.23	0.5857
27.0	317.16	0.5677
27.4	315.16	0.5641
29.0	310.09	0.5551
29.4	308.15	0.5516

To express the kinematic viscosity in equation form, the data collected was fit to the following equation:

Kinematic viscosity (Centistokes) = 1.0045E-7 * T^3 +9.6723E-5 * T^2 -0.012046 * T + 0.81991

where T is the Celsius temperature. Variations in gravitational acceleration between the place where the viscometer was calibrated (New Jersey) and used (Alabama) were assumed to be negligible (ASTM D 445 paragraph 8.3). Standard error for the viscosity as determined from a polynomial fit of the data was 0.0012 centistokes.

4.6.3 Viscosity of Chloropicrin

To determine the absolute viscosity of chloropicrin, an equation for the density of chloropicrin had to be determined first. To develop this equation, the density of chloropicrin was measured at 5-degree intervals from 0°C to 30°C (Table 4-14) and the data was fitted to a polynomial equation. The measured density of the chloropicrin used was lower than values recorded in the literature (1.6558g/ml at 20°C and 1.6483g/ml at 25°C or about 0.7 or 0.8% difference for both). Uncertainty in the volume measurements was on the order of plus or minus 0.01 ml. However, some loss of chloropicrin was noted over the course of the test, amounting to 0.5%. To express the kinematic viscosity in equation form, the data collected was fit to the following equation:

Density (g/ml) = -2.458E-6 * T^3 +1.5234E-4 * T^2 -0.004304 * T -1.6888

where T is the Celsius temperature.

To obtain absolute viscosity in centipoise, the values from the two curves were multiplied together at a given temperature.

Viscosity (in centipoise) = kinematic viscosity (in centistokes) * density (g/ml) = (1.0045E-7 * T^3 +9.6723E-5 * T^2 -0.012046 * T + 0.81991) * (-2.458E-6 * T^3 +1.5234E-4 * T^2-0.004304 * T-1.6888)

Table 4-14

Determination of the Viscosity of Chloropicrin - Temperature, Volume, and Density Data from Laboratory Testing

Temperature (°C)	Volume (ml)	Density[1] (g/ml)
0.7	4.91	1.686
5.3	4.96	1.669
10.5	5.00	1.656
15.3	5.01	1.653
20.6	5.04	1.643
25.3	5.06	1.636
30.6	5.08	1.630

(1) The estimated uncertainty in the density measurement is slightly greater than 0.5%.

Uncertainty from the density measurement overrides uncertainty from the kinematic viscosity measurement. Total uncertainty in the calculated absolute viscosity (in centipoise) is estimated to be on the order of 0.7%. Table 4-15 lists the viscosity and density of chloropicrin at several temperatures.

4.7 DSITMS Method Development

ORNL was contracted to develop a rapid analytical method for the CNS components using DSITMS. This method involves either direct purge of discrete 40-ml samples of water or soil or direct (*in-situ*) analysis of water samples in groundwater wells using a specially designed sampling probe. A detailed report describing the analytical method development and a summary of the method is provided in Appendix D. The following summarizes the results of the study.

Experiments using authentic standards of chloroform and chloropicrin clearly demonstrated that these two compounds can be detected at ambient temperature in water at concentrations of less than 5 ppb using either the 40-ml VOA vial sparging method or the *in-situ* sparging probe. Using the 40-ml VOA sparging method, both of these compounds can be quantitated in water or soil samples using a 3-minute analysis time. The total time required to quantitate these compounds by the *in-situ* sparging method is approximately 5 to 15 minutes per groundwater well. If depth profiling is performed, it currently requires approximately 1 minute per foot of depth over the interval that is profiled.

In order to detect phenacyl chloride in water at a concentration of less than 50 ppb, it was necessary to use the 40-ml VOA vial sparging method while heating the sample to 60°C. The time required for quantitation of this compound was approximately 15 minutes. Phenacyl chloride is not considered suitable for *in-situ* sparge analysis for two reasons: the analysis time exceeded the 3 minute limit selected as suitable for rapid field measurements, and there was no practical way to heat the sample while being purged.

Table 4-15

Viscosity and Density of Chloropicrin Between 0 and 29.4°C

Temperature (°C)	Density (g/ml)	Absolute Viscosity (Centipoise)
0.0	1.69	1.38
4.9	1.67	1.28
10.5	1.66	1.16
15.0	1.65	1.09
20.3	1.64	1.01
24.3	1.64	0.96
29.4	1.63	0.90

To ascertain the accuracy of the DSITMS method for analyzing chloroform and chloropicrin in discrete water samples, two 40-ml blind spiked water samples (high and low concentration) for chloroform and chloropicrin were analyzed. For chloropicrin, the recovery was found to be in the range of 97%-106%, and for chloroform the recovery ranged between 89%-91%. The low-level chloropicrin and chloroform samples were spiked with 12.5 ppb of analyte. The concentrations that were found were 12.2 ppb and 11.1 ppb, respectively, corresponding to an error of 3% and 11%. The high-level performance samples were spiked with chloropicrin and chloroform to produce a solution concentration of 62.5 ppb for each analyte. The concentrations determined by DSITMS were 66.3 ppb for the chloroform and 56.7 ppb for the chloropicrin. This corresponds to an error of 6% and 9%, respectively, relative to the known concentrations.

Performance for soil was determined by analyzing soil samples that had been spiked with chloropicrin and chloroform. For this experiment, 5-g aliquots of a standard soil sample were spiked with 400 ppb of chloropicrin and chloroform. Because soil matrices are far more complicated than water in terms of the interaction with analytes, many compounds are not easily purged from soil or soil slurries. Therefore, the results showed a significantly lower recovery than the water results. For chloropicrin, the percent recovery ranged between 48%-58% and for chloroform the percent recovery ranged between 24%-30%. For this reason, calibration curves for soil analysis should be generated using a soil type that is very similar in composition to the soil from the site where the samples are collected.

For laboratory-based screening and quantitative analysis applications, 40-ml discrete sample sparging can be used effectively. In the field, it is also possible to utilize the *in-situ* sparging probe for the analysis of chloroform and chloropicrin in groundwater wells. Detection limits are in the range of 5 ppb for water samples, and the precision is typically better than +/- 10%. Soil samples are more difficult to analyze than water samples and have a recovery of as little as 25% of that for the same compounds in water. Detection limits are in the 5 ppb range for chloroform and chloropicrin in soil but are expected to vary with the specific type of soil.

4.8 Borehole Flowmeter Demonstration

The borehole flowmeter tests revealed that groundwater flow beneath Area 15A is dominated by a few thin flow paths while there is only minor flow through the porous rock matrix. Discrete flow measurements were taken in eight wells. Except for well TVA-1, which was installed to a depth of 90 feet to permit the measurement of hydraulic conductivity in both the Saltsburg and Buffalo Sandstone aquifers, the measurements were limited to the lower few feet of soil overburden and the upper 10 to 20 feet of the sandstone and shale associated with the Saltsburg formation. Of the 165 discrete hydraulic conductivity estimates that were obtained from borehole flowmeter tests, 55% of the measurements were below the measurement threshold. Horizontal hydraulic conductivity values for the 74 measurements which exceeded the measurement threshold ranged from 1.4×10^{-5} to 0.2 cm/s. Since all of the test wells are vertically oriented, it is inferred that the hydraulic conductivity values are primarily associated with horizontal fractures intersected by the wells. However, vertical fracture sets undoubtedly exist at the site due to past tectonic activity. The anticlinal structure of bedrock underlying Area 15A suggests the likelihood of vertical tension fracture sets. The borehole flowmeter testing of Area 15A is described in detail in Appendix E of this report.

4.9 Modeling of Natural Restoration of Bedrock Aquifer

The soil in Area 15A consists of a 3-meter thick layer of residual silty/sandy clay soil. Below this layer of soil is the Glenshaw formation, which consists of layers of fractured and interbedded sandstone, shale, and thin coal seams. Water at the soil surface migrates downward through the drum burial zone into the underlying bedrock. Once in the bedrock the groundwater moves both downward and southwesterly, flowing primarily through a sparse network of hydraulically active fractures. A limited amount of the groundwater flows through the formation's low permeable rock matrix. The groundwater ultimately discharges along the bedrock outcrops, forming seeps located less than 200 meters west of Area 15A

To determine if remediating the soil overburden would significantly reduce the amount of time required for restoring the underlying bedrock aquifer to its natural state, a finite element computer model was used. Two restoration scenarios were evaluated:

- A soil remediation scenario in which it was assumed that all of the CNS components would be removed from the soil by the year 2000.
- A no-action scenario in which natural restoration of the site was allowed to occur without actively remediating the soil overburden.

In both scenarios, it was assumed that the aquifer would undergo natural restoration.

Only the behavior of chloroform was modeled because:

- Site characterization studies revealed that chloroform was by far the most persistent of the site's three CNS compounds.
- Chloroform is the primary regulatory concern.
- The modeling code could evaluate only a single contaminant at a time.

The simulations were run assuming a chloroform mineralization half-life of 277 days based on a preliminary evaluation for the mineralization half-life data. This figure was slightly higher than the 227 day half-life developed after fully evaluating the mineralization data. Although the modeling results were highly sensitive to chloroform degradation rates, the use of the higher number is not thought to have significantly affected the study results. In part, this is true because the model has accurately predicted the concentrations of chloroform coming out of the bedrock seeps when the 277 day figure was used. For evaluating the model's sensitivity to chloroform degradation rates, runs were also made with chloroform half-lives of 0 and 1,800 days. The computer model's predictions were also slightly sensitive to fracture distribution.

Using the 277 day figure, the model indicated that soil remediation had essentially no impact on aquifer restoration time. With or without soil remediation, the chloroform concentrations at the discharge boundary are expected to fall below the maximum concentration limit of 10^{-4} g/L by the year 2010. Furthermore, the model predicted that all of the chloroform should be

degraded by the year 2050.

Using the substantially more conservative 1,800 day mineralization half-life indicated that the seep concentrations should be well above those being observed. Under this scenario, the model indicated that the concentrations of chloroform at the discharge boundary would fall below the maximum concentration level of 10^{-4} g/L by the year 2075 and that essentially all of the chloroform stored in the bedrock would be depleted by the year 2100.

All simulations considered in the modeling analyses indicated that the highest chloroform levels have been observed at the site and that improving conditions can be expected in the future. A detailed report of the bedrock aquifer modeling work is provided in Appendix F.

As with all modeling, the results described above are subject to the assumptions used during modeling. Key uncertainties and assumptions included:

- The exact number of drums buried at the site is unknown. The upper end of the range, 1,700, was used in the modeling work. Other inputs for the modeling work were based on the best available information.

- Soil properties were based on soil samples taken from undisturbed soil near and adjacent to the landfill. The properties of the landfill soil may have been altered by excavation and back-filling.

- The estimate of fractures in the bedrock was based on borehole flowmeter measurements of wells. Due to the lack of deep wells, these measurements are limited primarily to the uppermost aquifer. Vertical fractures had to be inferred since all groundwater flow measurements were made in vertical wells and borehole data on vertical fractures were not available.

- Sampling of the seeps has been limited to a few quarterly sampling events and the minimum detection limits for chloropicrin have often been too high to verify the absence of this compound in the seeps.

- Very few of the wells were deep enough to measure the quality of groundwater beneath the uppermost water-bearing stratum. A recent characterization of groundwater farther down-gradient than previous investigations revealed that the contaminant plume may have a more southerly component than previously predicted.

4.10 Evaluation of Remedial Strategies

4.10.1 General Observations

It was considered prudent to investigate alternative remediation strategies for Area 15A for two reasons:

1) The alternatives considered for this site may be applicable to other military sites with CNS tear gas contamination.
2) Prior to conducting this study, it was thought that remediation of the soil or groundwater might shorten the required duration of the targeted pump and treat activities.

However, it should be noted that the complex geology and soil properties of Area 15A make the site a poor candidate for active remediation of both the soil and/or the groundwater/bedrock. The site is a poor candidate for soil remediation because it is believed that the majority of the tear gas is no longer in drums and has infiltrated the fractured bedrock. In addition, the soil in the drum burial area is poorly suited for many remedial technologies due to its low permeability and, as indicated in Section 4.10 above, computer modeling of the site indicates that soil remediation will have essentially no impact on aquifer restoration time. Finally, since the CNS components are denser than water, any strategy that mobilizes the soil contaminants risks speeding their downward movement into the bedrock and its associated aquifer.

Groundwater remediation would also be difficult because the contaminants move through the bedrock through a complex network of discrete fractures and are also absorbed into the rock matrix. While attempts to remediate the groundwater/bedrock may efficiently treat those contaminants within the fractures, the contaminants within the rock matrix are largely untreatable because they are located within rock with low permeability.

4.10.2 Evaluation of Soil Remedial Strategies

4.10.2.1 Assessment of Soil Remediation Alternatives

In assessing the soil remediation alternatives, a number of alternatives were considered for use at Area 15A (Table 4-16). These options were initially screened and assessed in terms of their perceived technical feasibility, short- and long-term risks, and cost (Table 4-17).

After extensive evaluation (Appendix G), a number of the remediation technologies were rejected (Table 4-18). In general, all of the *ex-situ* technologies were rejected due to health risks and high cost. In addition to the health risks associated with exposure to tear gas compounds, possible exposure to phosgene was a significant consideration. Phosgene is a possible degradation product of both chloroform and chloropicrin and is a particularly insidious poison. Although phosgene is an extremely toxic compound, fatal concentrations may be inhaled without being immediately irritating.[Ref. 23] Cost was also a significant factor since 33,400 cubic yards of soil would have to be treated at an estimated cost of about $15M for off-site treatment and disposal or about $14M for on-site treatment and disposal. This was equivalent to unit cost of $420 to $450 per cubic yard of soil which is comparable to other estimates.

The *in-situ* technologies which appeared to merit further consideration were then rated for relative applicability, availability, cleanup times, and cost (Table 4-19). The ratings for applicability took into account site-specific limitations. For example, Soil Vapor Extraction (SVE) is normally recommended for remediating VOCs. However, the low permeability of the soil around Area 15A makes this technology less applicable to this site. The availability rating was based on the number of experienced vendors available to design, construct, and maintain the technology. A rating of 1 means that at least 5 vendors were available, a rating of 2 means that 3 to 5 vendors were available, and a rating of 3 means that fewer than 3 vendors were available.

Table 4-16

Soil Treatment Technology Considered for Use at Area 15A

Technology	Description
***Ex-situ* Soil Treatment Technologies**	
Landfill Disposal	This involves excavation and treatment (depending on the contaminants involved) and disposal in an approved RCRA landfill.
Thermal Desorption	*Ex-situ* process where VOCs and SVOCs are removed by heating the soil. A carrier gas or vacuum system transports contaminants to the gas treatment system.
Incineration	High temperatures (900-1,200°C) are used to combust organic constituents in the soil in the presence of oxygen,
***In-situ* Soil Treatment Technologies**	
Enhanced Bioremediation	The activity of naturally occurring microbes is stimulated by circulating water-based solutions through the contaminated soil. Nutrients, oxygen, pH adjusters, and other additives are used to enhance biodegradation and desorption of contaminants.
Chemical Treatment	Involves the addition of water-based additives to either oxidize or reduce contaminants. Typical oxidizers used are ozone, peroxide, or potassium permanganate. The most common reducing agent is sodium dithionite.
Natural Attenuation	Natural subsurface processes such as dilution, volatilization, biodegradation, adsorption, and chemical reactions with subsurface materials are allowed to reduce contaminant levels to acceptable levels.
Soil Vapor Extraction (SVE)	Vacuum is applied through extraction wells to create a pressure/concentration gradient that induces gas-phase volatiles to diffuse through the soil to the extraction wells.
Thermally Enhanced SVE	Electrical resistance heating, electromagnetic heating, hot air, or steam is used to increase the volatilization of SVOCs and VOCs to facilitate extraction.

Table 4-17

Comparison of Soil Treatment Technologies

Treatment	Short-Term Risk	Long-Term Risk	Stage of Development	Relative Cost[1]
***Ex-situ* Soil Treatment Methods**				
Landfill Disposal	High	Low	Fully developed	High ($405-690/cu yd)
Thermal Desorption	High	Low	Fully developed	High ($60-$450/cu yd)
Incineration	High	Low	Fully developed	High ($200-$1,000/ ton)
***In-situ* Soil Treatment Methods**				
Enhanced Bioremediation	Low	Medium	Treatability studies required	Low ($20-$80/cu yd)
Chemical Oxidation/Reduction	Low	Medium	Few vendors available	Medium
Natural Attenuation	Low	High	Modeling required	Low
Soil Vapor Extraction (SVE)	Low	Low	Fully developed	Low ($10-$40/cu yd)
Thermally Enhanced SVE	Low	Low	Pilot scale	Medium ($25-$100/cu yd)

(1) Cubic yard of soil is assumed to weigh 1.5 tons.[Ref. 24]

Table 4-18

Treatment Technologies Rejected

Technology	Reason for Rejection
***Ex-situ* Soil Treatment Methods**	
Landfilling	High cost and high short term risk
Thermal Desorption	High cost and high short term risk
Incineration	High cost and high short term risk
Ex-situ Bioremediation	High operating and maintenance cost and short term risk
Ex-situ Chemical Treatment	Short term risk
Ex-situ Chemical Extraction	Relatively high cost and short term risk
***In-situ* Soil Treatment Methods**	
In-situ Solidification	High cost and limited effectiveness for contaminants of concern
Capping	Site hydrogeology not suitable for technology
Barrier Walls	Site hydrogeology not suitable for technology
In-situ Vitrification	High cost and technology unproven on the scale required for Area 15A

Table 4-19

Technology Screening Matrix for *In-situ* Soil Treatments

Technology	Rating[1]				
	Applicability[2]	Availability[3]	Cost	Cleanup Time	Total Score[4]
***In-situ* Biological Treatment**					
Bioventing	3	1	1	3	8
Enhanced Aerobic Bioremediation[5]	2	2	2	3	9
Anaerobic Bioremediation	2	3	2	3	10
Enhanced Biological/Chemical Degradation	2	2	2	2	8
Monitored Natural Attenuation	1	1	1	3	6
***In-situ* Physical/Chemical Treatment**					
Electrokinetic Extraction	3	3	3	3	12
Extraction Aided by Fracturing	2	3	2	2	9
Soil Flushing	3	1	3	3	10
Soil Vapor Extraction (SVE)	3	1	1	2	7
Chemical Oxidation	2	3	2	2	9
Chemical Reduction	2	3	2	2	9
***In-situ* Thermal Treatment**					
Thermally Enhanced SVE[6]	2	3	2	1	8

(1) Ratings: 1=better, 2=average, 3=worse
(2) The ratings for applicability took into account the site-specific limitations.
(3) Availability refers to the number of vendors that could design, construct, and maintain the technology. A rating of 1 means that there are at least 5 vendors, 2 means that there are 3 to 5 vendors and 3 means that there are fewer than 3 vendors for the technology.
(4) The total score is the sum the individual ratings. The lowest scoring technologies are those most suited for use at Area 15A.
(5) Additives include air sparging, magnesium peroxide, ozone, and hydrogen peroxide.
(6) Heating done by injecting hot air or by injecting hot air while mixing soil with an auger.

Finally all of the technologies in Table 4-19 were individually evaluated. Of these alternatives, three were considered viable for use in Area 15A:

- Monitored Natural Attenuation
- Enhanced Biological/Chemical Degradation (an *in-situ* option)
- Thermally Enhanced Solvent Vapor Extraction (an *in-situ* option)

4.10.2.2 Assessment of Monitored Natural Attenuation

Of the approaches examined, Monitored Natural Attenuation had the highest rating in terms of applicability and overall score (Table 4-19). There are several reasons for this high rating.

- In the current setting, the tear gas components pose little risk to the environment.
- Deed restrictions and institutional controls can prevent human exposure to the landfill area.
- The low concentrations and volatility of chloroform are such that it is unlikely to persist in surface water.
- The remaining two compounds are not being detected in seep water.
- It is exceptionally difficulty to remediate contaminants diffused into the bedrock matrix.

In addition to these factors, computer modeling indicates the CNS components may be nearly completely degraded in the near future. Exploratory trench investigations in 1985 revealed that 90 percent of the drums had deteriorated.[Ref. 25] A second investigation in 1995 found no intact drums.[Ref. 26] Using the assumption that 90% of the drums were deteriorated by 1985, the results of the modeling effort (see Section 4.9) indicate that there will be no tear gas within the soil overburden by the year 2000 and that chloroform stored in the bedrock should be flushed out or degraded by the year 2050.

In view of the difficulty associated with remediating contaminants diffused into the bedrock matrix, natural attenuation merits consideration. However, further characterization of the seeps down-gradient of Area 15A is needed to quantify the amount of CNS-derived contaminants reaching surface water and to assess the risk of this surface water contamination.

4.10.2.3 Assessment of Enhanced Biological/Chemical Degradation

Should natural attenuation not prove to be an attractive option, then one of the *in-situ* degradation processes will have to be employed. Among the *in-situ* degradation processes, the Enhanced Biological/Chemical Degradation process, a combination of biological and chemical degradation, was considered the optimal approach for Area 15A.[Ref. 27] In Enhanced Biological/Chemical Degradation, certain soil amendments and other biodegradable chemicals are added to soil to enhance the natural rate of biological and chemical degradation. The chemicals involved are usually common agricultural chemicals such as fertilizers, agricultural bases, etc., and carbon sources such as methanol, methane, and propanol. The carbon sources normally serve as a food source for the microbial population.

Among the most important considerations for recommending Enhanced Biological/Chemical Degradation was its relative simplicity and applicability for use at Area 15A. Because of the acidity of the soil within Area 15A, it had already been established that microbial degradation at the site could be enhanced if the soil pH was raised above neutral by the addition of a chemical base. Coincidentally, two of the CNS components, chloropicrin and phenacyl chloride, were also known to be easily hydrolyzed by bases. Moreover, it was known that rapid microbial degradation of chloroform will be possible if the growth of microbial methylotrophs or nitrifiers is encouraged. For example, the organism *Methylosinus trichosporium-Ob-3b* has been shown to oxidize chloroform with a reaction half-life of about 0.5 hour.[Ref. 28] Furthermore, if ammonium hydroxide was used as both the chemical base and a nitrogen source, then the rate of chloropicrin and phenacyl chloride hydrolysis could be enhanced while the rate of chloroform degradation is being enhanced (by encouraging the growth of nitrifying bacteria). Lime or another base may be substituted for ammonium hydroxide; however, these materials are inferior in terms of their ability to penetrate the soil.

Methanol was considered the preferred carbon source because chloroform degrading methylotrophs metabolize methanol. Methanol's solubility in water and chloroform was also a consideration. Methanol is soluble in both water and chloroform and can serve as a carrier for ammonia and ammonium hydroxide. Methane may be substituted for methanol, but it is inferior since it is not as soluble in water. Propanol can also be used but is more expensive

than methanol, is not as good a solvent, and is not as readily metabolized by the methylotrophs.[Ref. 27]

As a consequence of the advantages described above, TVA considers Enhanced Biological/Chemical Degradation to be the preferred means of actively reducing the CNS contaminant concentrations in the soil overburden. Should this method be employed, then the use of ammonium hydroxide and methanol additives are recommended to enhance the natural rate of biological and chemical degradation.

4.10.2.4 Assessment of Thermally Enhanced Solvent Vapor Extraction

Another viable *in-situ* degradation process is Thermally Enhanced Solvent Vapor Extraction. Thermally Enhanced Solvent Vapor Extraction is a process in which heated air is passed through the contaminated soil while a vacuum is placed over the soil to capture any volatile compounds given off. To treat Area 15A's soil, this can be accomplished by mixing the soil with a large-diameter vertical auger while injecting hot air into the soil. The auger would be equipped with a shroud and vapor recovery system to capture the volatile contaminants. The main advantages of this approach are that it is simple, can be accomplished in a relatively short time, and can be implemented in low permeability soils like those existing in Area 15A. During bench-scale studies using the vertical auger technique combined with hot air injection at 100°C, 99% chloroform removal was achieved when combined with SVE methods.[Ref. 29] Eighty-five percent of this chloroform was removed with hot air only. The estimated cost of combining soil mixing, hot air injection, and SVE is $75 per cubic yard. This technique can also be modified to include the mixing of a base into the soil, as a means of encouraging the hydrolysis of chloropicrin and phenacyl chloride. Base addition would raise treatment cost to around $100 per cubic yard. While the bench scale study results are promising, it should be noted that an unrealistic amount of hot air was used in the bench-scale tests. About 2,000 soil-pore-volumes of hot air were passed through the soil. In addition, like other extraction methods, this strategy has the problems associated with disposal or treatment of the contaminants.

It should also be noted that Thermally Enhanced Solvent Vapor Extraction, in combination with pneumatic fracturing, is the only technology reported to successfully treat dense

non-aqueous phase liquids (DNAPLs) in fractured bedrock.[Ref 30] This was accomplished on a less broad but deeper plume than the one at Area 15A. Also, there was much less contaminant, about 500 gallons versus the possible 15,000-85,000 gallons at Area 15A. The cost per pound of DNAPL removed was quite high, but the urban setting and high value of the land justified the high cost in the case reported.

4.10.2.5 Assessment of Other Soil Remediation Methods

A thorough assessment of the soil remediation methods examined can be found in the document in Appendix G.

4.10.3 Evaluation of Groundwater Remedial Strategies

4.10.3.1 Underlying Chemical, Hydraulic, and Geologic Considerations

Knowing the chemical and physical properties of the chemical contaminants at a site is essential to developing groundwater remedial strategies. For the purpose of screening potential technologies, CNS tear gas compounds can be placed into one of two classes of chemicals:

- Halogenated volatile organic compounds
- Halogenated semivolatile organic compounds

Chloroform and chloropicrin are considered halogenated volatile organic compounds and phenacyl chloride is a halogenated semivolatile organic compound. Due to their differing water solubilities, susceptibility to biological degradation, and volatility in air, these compounds were expected to separate with the passage of time.

Analysis of soil and groundwater in the drum burial area indicates the compounds have in fact separated. Due to phenacyl chloride's low solubility in water, measured concentrations in groundwater are much lower than the other two compounds.

Chloroform, the least biodegradable of the three compounds, is found in the highest concentrations in the groundwater down-gradient of the landfill and at low concentrations in

Tributary B. A groundwater treatability study conducted in 1987 concluded that indigenous organisms at the site were capable of degrading the contaminants but were inhibited by either low pH or toxicity of some of the contaminants.[Ref. 31] These findings supported Castro's assertion that low pH has impeded degradation of the contaminants.[Ref 32] Also in this study, sewage treatment plant organisms were added to the groundwater to enhance biodegradation. The study concluded that microbial growth in groundwater could be enhanced by either neutralization or dilution.

Limited upward diffusion of the volatile contaminants is also thought to have occurred through the soil vadose zone resulting in contaminant losses to the atmosphere. Volatile losses are most likely for chloroform and, to a lesser extent, chloropicrin and chloroacetophenone. Overall vapor losses are expected to be small since the vapor densities of these compounds (which range from approximately 4.1 to 5.7) greatly exceed that of ambient air, indicating a tendency for vapors to sink rather than rise in the vadose zone. Vapor losses may be enhanced by seasonal water table fluctuations which may force vapors to the surface as rising water displaces soil vapors.

Due to physical nature of the contaminants, they can exist in four phases within the subsurface soil/bedrock matrix:

- Gas/vapor phase - usually present in the unsaturated zone
- Solid phase - present in liquid or solid form and adsorbed on soil particles in both the saturated and unsaturated zone
- Aqueous phase - dissolved into pore water or groundwater according to solubility
- Immiscible phase - present as DNAPLs (i.e., dense non-aqueous phase liquids)

The bulk of the CNS tear gas components present in the bedrock at Area 15A are thought to be present as immiscible DNAPLs. Consequently, the contaminants' rate of movement through the soil, bedrock, and groundwater is defined by the behavior of these DNAPLs. Groundwater flow measurements in the fractured bedrock beneath Area 15A indicate that groundwater movement through the Saltsburg Sandstone is dominated by a few thin preferential flow zones[Ref. 33] with hydraulic conductivity in these thin zones being high as 0.2 cm/sec. Consequently, groundwater and DNAPL movement is defined by a relatively sparse network of

hydraulically active fractures. The rate and direction of this movement is defined by the size, orientation, and connectivity of the fractures and by prevailing hydraulic gradients.

Theoretically, the contaminants could also flow through the rock matrix; however, hydraulic conductivity of the porous sandstone-shale matrix in and around Area 15A is very low. Indeed, the rock matrix is more likely to act as an reservoir and inhibit rapid component movement through the aquifer. This is likely because upon entering the fractures, relatively soluble DNAPL compounds such as chloroform are likely to diffuse into (and out of) the rock matrix as they are transported with ambient groundwater. Migrating DNAPL may also become disconnected or trapped by capillary forces in narrow fractures forming zones of residual product. These regions of residual product and rock matrix contamination result in persistent sources of dissolved-phase contamination within the bedrock. Further complicating the situation, solid phenacyl chloride is likely to precipitate from DNAPLs containing low concentrations of chloroform and chloropicrin. This is likely to inhibit the removal of phenacyl chloride. Because of the contaminant's tendency to diffuse into the rock matrix, become trapped in narrow fractures, and phenacyl chloride's tendency to precipitate out of solution, Area 15A site is a poor candidate for groundwater treatment.

4.10.3.2 Feasibility of Using Selected Groundwater Remediation Methods at Area 15A

There are several ways to remediate groundwater or prevent further contaminant migration. These include:

- Low permeability caps or slurry walls (to contain the contaminants)
- *In-situ* solidification (to isolate the contaminants)
- *In-situ* vitrification (to degrade contaminants)
- *In-situ* treatment (to degrade contaminants)
- *Ex-situ* groundwater pump and treat (to contain and degrade contaminants)
- Monitored natural attenuation

In-situ vitrification was rejected as an option because of cost and because it is still in the early stages of development. *In-situ* vitrification involves the heating of the soil using electrical

current. It is relatively expensive ($300-$450 per ton) and has not been conducted commercially.

Most of the remaining options cannot be implemented at Area 15A due to site characteristics or the nature of the contaminants. For example, containing the contaminants either by capping the site or using barrier walls would not be a practical option at Area 15A since the fractured nature of the bedrock beneath Area 15A and the resulting high hydraulic conductivity would make it exceptionally difficult to contain the contaminants. Similarly, the use of solidification would not be an appropriate option for this site since solidification is unable to effectively isolate VOC's like those found in Area 15A. Solidification refers to the mixing of cementitious materials using an auger. The technique is primarily used to isolate inorganic contaminants.

In-situ treatment methods would be effective if the contaminants were only in the groundwater. Unfortunately the contaminants have become embedded in the bedrock's internal pore space. Because the contaminants must overcome capillary pressures to escape the rock matrix, it will take a long time for the contaminants to diffuse out of the bedrock and into the groundwater where they can be treated. For example, computer simulations predict that it may take about 200 years to naturally flush the existing chloroform out of the Area 15A's bedrock if degradation is not assumed to occur and 50 years if degradation is assumed to occur (Appendix F). Given these timeframes, it would be difficult to justify an *in-situ* groundwater treatment strategy.

Ex-situ pump and treatment is a viable option if the goal is limited to preventing contaminant migration. However, as with the *in-situ* treatment methods, e*x-situ* treatment of the groundwater in not likely to result in an enhanced remediation rate due to the presence of contaminants in the rock matrix.

4.10.3.3 Existing Groundwater Remediation Plans

In response to the Pennsylvania Department of Environmental Resources' (PADER) concern regarding the offsite migration of chloroform, TransTechnology Corporation is currently developing a remedial strategy. The goal of this strategy, referred to as the targeted pump and treat, is to prevent CNS contaminants in the groundwater from reaching Elders Run by intercepting the groundwater and treating the contaminants prior to discharging the groundwater. To implement the strategy, an array of extraction wells would be installed to intercept the groundwater from the uppermost aquifer (Saltsburg Sandstone). The wells would be positioned to assure that the groundwater is intercepted before it reaches discharge seeps and would be oriented north to south. An *ex-situ* treatment system is proposed to either degrade the contaminants in the liquid phase or remove them from the water and treat them as a vapor. A key element of the strategy is the positioning of extraction wells down-gradient of the contaminant source and near the point of surface discharge (the seeps). At this location, the concentration of contaminants in groundwater should be much lower than near the source, thus reducing the size and complexity of the water or off-gas treatment system. The location of the proposed targeted pump and treat system is on property adjacent to the Federal Laboratories boundary.

To design the targeted pump and treat system, a groundwater investigation was conducted in 1998 to determine the extent of the contaminant plume in the vicinity of the proposed extraction wells. The investigation entailed the installation of five upper zone and two middle zone wells southwest of Area 15A on the adjacent property. Results of the investigation indicated that the plume has a more southerly component than predicted. The implication is that the array of extraction wells will need to extend farther south than was originally anticipated. At the time of this writing, TransTechnology Corporation was awaiting a response from PADER regarding the results of the groundwater investigation.

4.10.3.4 Assessment of Alternate Groundwater Remediation Options

In assessing groundwater remediation alternatives, a number of *in-situ* and *ex-situ* options were considered for use at Area 15A (Table 4-20). These alternatives were considered primarily as a means of augmenting TransTechnology Corporation's proposed pump and treat system and

Table 4-20

Groundwater Treatment Technologies

Technology	Description
***In-situ* Groundwater Treatment Technologies**	
Co-Metabolic Treatment	Injection of liquids or gases (e.g., toluene, methane or methanol) to enhance the rate of methanotrophic degradation of organic contaminants.
Enhanced Biodegradation	The rate of biodegradation of organic contaminants is enhanced by providing nutrients, electron acceptors, and competent degrading microorganisms.
Natural Attenuation	Natural subsurface processes such as dilution, volatilization, biodegradation, adsorption, and chemical reactions with subsurface materials are allowed to reduce contaminant levels.
Chemical Oxidation	Strong oxidizers are injected in the groundwater to oxidize organic contaminants.
***Ex-situ* Groundwater Treatment Technologies**	
Air Stripping	Volatile organics are partitioned away from groundwater by increasing the surface area of groundwater exposed to air.
Sprinkler Irrigation	Groundwater is distributed through a sprinkler irrigation system to volatilize contaminants.
Granulated Activated Carbon Adsorption	Groundwater is passed through columns containing activated carbon to which organic contaminants are adsorbed.
Ozonation	Contaminated water and ozone are passed through a packed bed reactor containing activated carbon which acts as a catalyst as contaminants are oxidized by oxygen radicals.

emphasis was placed on ensuring that these systems could be incorporated into the proposed pump and treat system.

As indicated in Section 4.10.3.2, treatment times are likely to be extremely long in the fractured bedrock found beneath Area 15A. Given the timeframes involved, it is difficult to justify any of the *in-situ* groundwater treatment strategies listed in Table 4-20, and their use is not recommended. However, should it be considered desirable to attempt *in-situ* remediation, then the *in-situ* processes listed in Table 4-20 could be positioned up gradient from the proposed extraction wells in an effort to reduce contaminant concentrations.

The recommended groundwater remediation methods are: Monitored Natural Attenuation and plume containment by groundwater extraction and treatment. Of these two options, the Monitored Natural Attenuation option is preferred because Area 15A's complex geology makes it unsuitable for pump and treat technologies and because there is strong evidence that the CNS components are degrading. However, it would be appropriate to better quantify the amount of CNS-derived contamination likely to reach the surface before implementing this option.

Should the use of Monitored Natural Attenuation be deemed unacceptable by the parties involved, then the *ex-situ* groundwater pump and treat option proposed by TransTechnology Corporation is likely the only other practical alternative. This strategy would involve the placement of extraction wells near the points of discharge (surface seeps west of the site). However, to accurately place the extraction wells, it is recommended the contaminant plume be better delineated. Should this option be adopted, then it is recommended that the least costly treatment system available be used to minimize operating and maintenance costs, since the system may need to be operated for several decades.

Additional details supporting these evaluations may be found in the document in Appendix G.

4.11 Evaluation of Injection/Recovery Alternatives

Eight different delivery/recovery alternatives for treating the soil overburden were evaluated using numerical modeling analysis (Table 4-21). These systems would most likely be used if a decision was made to remediate the soil overburden with the *in-situ* enhanced biological/chemical degradation process (see Section 4.10.2.3).

Injection methods examined included:

- Injection trenches
- Shallow injection wells
- Infiltration galleries

A detailed report of the injection and recovery system simulations is provided in Appendix H.

Recovery methods examined included:

- Horizontal wells
- Trenches
- Vertical wells

Criteria used to evaluate these systems included:

- Hydraulic efficiency
- Effective delivery of treatment agents to contaminated soil
- Minimizing contaminant migration
- Project life

For delivering additives to the soil, infiltration galleries were found to be superior to injection trenches and shallow injection wells because it allowed higher influx rates and provided better distribution of additive in the soil. Delivery by shallow well injection was limited by the assumed hydraulic conductivity of the soil overburden ($5x10^{-6}$ cm/s). Modeling with the

Table 4-21

Injection/Recovery Scenarios Examined

Scenario	Injection / Recovery Method
1	Base Case (No Remedial Controls)
2	Injection Trench with Extraction Trench/
3	Injection Wells with Extraction Trench
4	Injection Wells with Vertical Extraction Wells
5	Infiltration Gallery with a Perimeter Extraction Trench
6	Infiltration Gallery with Vertical Extraction Wells
7	Infiltration Gallery with Longitudinal Horizontal Extraction Wells
8	Infiltration Gallery with Latitudinal Horizontal Extraction Wells

infiltration galleries indicates that 1.3 pore volumes per year of aqueous-based additive could be added to the soil overburden. This is an order of magnitude greater than alternatives relying on vertical wells or trench systems. Model simulations also suggested that increases in artificial recharge rates could be obtained by increasing the hydraulic conductivity of soil overburden at the burial site using methods such as induced fracturing or mechanical tilling. However, use of these options may enhance vertical migration of the contaminants and would likely promote contaminant release into the atmosphere.

To recover the soil additives, horizontal wells were found to be superior to trenches and vertical wells. Model predictions indicated that over 80% of the additive introduced by an infiltration gallery would be extracted if the horizontal wells were placed perpendicular to the natural (westerly) hydraulic gradient. This alignment adds redundancy to the extraction system and also allows adjustment to individual well extraction rates for increased control in the engineered hydrodynamics of the remediation system. The predicted concentrations of aqueous agent entering the underlying Saltsburg Sandstone was estimated to approach 5% of the initial concentrations after five years.

Due to the shallow depth of the soil, the horizontal wells could be installed using a "one-pass" trenching method. The technique relies on specialized trenching equipment that excavates a trench, supports the side-walls, inserts a well pipe in the trench, and then backfills the trench with selected media, all in one step. Cost estimates solicited from experienced contractors indicated that well installation costs are likely to range between $100,000 to $200,000. This estimate includes all costs for materials, mobilization, demobilization, and decontamination.

4.12 Project Quality Control Efforts

Measurement quality control efforts included laboratory measurements performed by both manual processes and automated devices such as chromatographs and autoanalyzers. These efforts were carried out using complete quality control activities as specified in Appendix C. These included proper calibration, calibration checks, use of independent check standards, matrix spikes, sample duplicates, and method blanks.

Quality assurance considerations were also included in project's experimental design. These efforts included:

- Where possible, the identity of synthesized compounds was checked against reagent grade material by comparing retention times on chromatography systems, and the purity of the synthesized compounds was also confirmed on appropriate chromatography systems.

- When two measurements existed to describe a characteristic, both measurements were used. For example, two methods for measuring soil particle size were used in this study.

- During the study, duplicate samples, multiple trials, controls, and blanks were included to ensure the integrity and correct interpretation of data for each portion of the project. For example, during the mineralization and soil sorption studies, a control container with all components but no soil was included in the studies.

A description of the project's QA program is provided in Appendix C.

SECTION 5.0
CONCLUSIONS

5.1 Background

Very little data are available which describe the fate of tear gas in soil or on the environmental processes which affect CNS tear gas as it moves through soil. To address this problem, the USAEC contracted with the TVA to conduct a three-phase study to examine the fate, transport, and effects of CNS tear gas in the soils of the Federal Laboratories Plant No. 3 in Saltsburg, Pennsylvania. Although the data collected are specific to the Saltsburg site, the data obtained should provide insight into the behavior of CNS tear gas at other sites.

Phase I of the Tear Gas Fate and Effects project consisted of a review of existing site characterization documents for Area 15A. In addition, borehole flowmeter technology was demonstrated during Phase I. The borehole flowmeter is an innovative site characterization technology that can be used to measure groundwater flow at discrete intervals in a well hole.

During Phase II, the TVA conducted a fate, transport, and effects study of CNS tear gas components in soil. The goal of Phase II was to obtain basic information about the behavior of soil-borne CNS tear gas. This information was used to model CNS behavior during Phase III. To the extent possible, Phase II built upon published information. However, some laboratory study was required to provide a theoretical basis for the conclusions reached.

In Phase III, TVA used the data collected in Phase II to model the transport characteristics of CNS in soil and bedrock and to investigate the potential use of innovative technologies to remediate tear gas contaminated sites.

5.2 Study Results

5.2.1 Results of the Fate, Transport, and Effects Study of CNS Tear Gas

The goal of the Fate, Transport, and Effects study was to obtain basic information about the behavior of soil-borne CNS tear gas. Most of the properties of the CNS components (phenacyl chloride, chloropicrin, chloroform) were taken from literature sources or were calculated using published information. However, laboratory testing was required to obtain some of the relevant information. A summary of CNS components' physical characteristics is provided in Table 5-1. Of these properties, those requiring laboratory testing included the:

- Individual component soil sorption coefficients
- Individual component half-lives in soil
- Individual component mineralization rates in soil
- Individual component mineralization half-lives in soil
- The viscosity and kinematic viscosity of chloropicrin

The soil sorption coefficients data indicated that chloroform and chloropicrin had similar soil sorption coefficients and that these values were about half the value for phenacyl chloride.

The component degradation and mineralization rates were much more difficult to determine than the sorption coefficients. During this test, the rate of component disappearance was much higher than was anticipated; consequently, the sampling interval used to test these rates was larger than would be preferred.

The test for component half-lives was based on the disappearance of each CNS component. The half-lives determined for chloroform, chloropicrin, and phenacyl chloride were 6, 6, and 36 days, respectively. However, these results may have been influenced by component volatility and sorption. Although measures were taken to minimize component losses during the half-life experiments, chloroform and chloropicrin may have been lost to volatilization. Both chloroform and chloropicrin are highly volatile compounds. Consequently, the degradation rates of chloroform and chloropicrin may have been exaggerated during the

Table 5-1

Summary of the Physical Properties of CNS Components

	Chloroform	**Chloropicrin**	**Phenacyl Chloride**
Chemical Formula	$CHCl_3$	CCl_3NO_2	$C_6H_5COCH_2Cl$
Molecular Weight	119.38 g/mol	164.37 g/mol	154.6 g/mol
Density	1.47 g/ml@ 20°C	1.66 g/ml @ 20°C	1.32 g/ml @ 15°C
Viscosity	0.58 cP	1.02 cP	Solid at room temp.
Water Solubility	8.2 g/L @ 20°C	1.5 g/L @ 22°C	<1 g/L
Melting Point	-63.5°C	-69.2°C	54°C
Boiling Point	61.2°C	112°C	244-245°C
Vapor Pressure	21.5 kPa @ 20°C	2.26 kPa @ 20°C	7.2×10^{-4} kPa @ 20°C
Vapor Density	1.05 g/L	0.15 g/L	4.56×10^{-5} g/L
Henry's Law Coefficient	0.13	0.10	$9.12\text{-}4.56 \times 10^{-5}$
Sorption Coefficient[1]	1.84	1.87	3.43
Component Half-Life[1]	6 days	6 days	36 days
Mineralization Rate[1]	-0.0025 day^{-1}	-3.33 day^{-1}	-0.11 day^{-1}

1) In soil from Area 15A

component half-life experiments. In addition, phenacyl chloride's tendency to be sorbed more strongly on soil particles makes it appear to be more prone to degradation relative to the other two compounds.

TVA is more confident of the accuracy of the experimentally determined mineralization half-lives because:

- The mineralization half-life experiments were conducted with labeled compounds, which made an accounting of the fate of the components easier to reconcile than in the component half-life experiments.

- The mineralization half-lives obtained were in better agreement with published values.

- Computer modeling using the mineralization half-lives produced results which were consistent with field observations in and around Area 15A (i.e., that chloroform is less prone to degradation and more recalcitrant than the other two components, that chloropicrin degrades faster than any of the other components, and that phenacyl chloride degrades at a slightly slower rate than chloropicrin).

The mineralization half-life experiments indicated that chloroform's degradation half-life is on the order of a few months (227 days) while the other two CNS compounds have half-lives on the order of a few days or less (0.21 and 6.3 days for chloropicrin and phenacyl chloride, respectively).

The measurements of viscosity and kinematic viscosity of chloropicrin were relatively straight forward and the related experiments were easy to conduct. At room temperature, chloropicrin was found to be more viscous than chloroform (1.03 centipoise versus 0.58 centipoise). Phenacyl chloride is a solid at room temperature and, therefore, is clearly not viscous at this temperature.

5.2.2 Results of the DSITMS Method Development Work

Both chloroform and chloropicrin can be analyzed using Direct Sampling Ion Trap Mass Spectrometry. DSITMS was found to be an unsuitable analysis method for quantifying phenacyl chloride due to the compound's low volatility and interaction with water.

5.2.3 Results of the Borehole Flowmeter Demonstration

The borehole flowmeter tests revealed that groundwater flow beneath Area 15A is dominated by a few thin flow paths while there is only minor flow through the porous rock matrix. Since all of the test wells are vertically oriented, it is inferred that the hydraulic conductivity values are primarily associated with horizontal fractures intersected by the wells. However, vertical fracture sets undoubtedly exist at the site due to past tectonic activity. The anticlinal structure of bedrock underlying Area 15A suggests the likelihood of vertical tension fracture sets.

5.2.4 Results of the Computer Modeling of Natural Restoration

All simulations considered in the modeling analyses indicated that the highest chloroform levels have been observed at the site and that improving conditions can be expected in the future. The modeling also indicates that remediation of the soil overburden would not impact aquifer restoration time. With or without soil remediation, the chloroform concentrations at the discharge boundary are expected to fall below the maximum concentration limit of 10^{-4} g/L by the year 2010. Furthermore, the model predicted that all of the chloroform should be degraded by the year 2050.

5.2.5 Results of the Evaluation of Remedial Strategies

5.2.5.1 Evaluation of Soil Remediation Strategies

The complex geology and soil properties of Area 15A make the site a poor candidate for active soil remediation. Consequently, Monitored Natural Attenuation is likely to be the best soil remediation option for the Area 15A site. This is likely because:

- Most of the CNS tear gas is no longer in the drums.
- There are difficulties associated with remediating contaminants diffused into a low permeable soil.
- In the current setting, the tear gas components pose little risk to the environment and deed restrictions and institutional controls can prevent human exposure to the landfill area.
- Computer modeling of the site indicates that soil remediation will have essentially no impact on aquifer restoration time (see Section 5.2.4).

However, should it be decided that a remediation of the soil overburden is desirable, then the best approach would be to combine both chemical and biological methods. The recommended strategy involves the injection of a chemical base and methanol into the soil. Methanol would be added to the soil to foster the growth of microbial methylotrophs which degrade hard to degrade chlorinated hydrocarbons like chloroform. The chemical base would be added both to encourage the hydrolysis of chloropicrin and phenacyl chloride and to stimulate the growth of nitrifying bacteria capable of degrading chloroform. Previous characterization studies have indicated that the CNS components have been degrading at the site, but that the degradation has been slowed by the acid conditions in the soil. The preferred base is ammonium hydroxide because of its capacity to stimulate microbial growth. Methods for injecting these chemicals into the soil are described in Section 4.11.

Another recommended method for remediating the soil is Thermally Enhanced Solvent Vapor Extraction. This process involves vacuuming volatile compounds out of the soil while mixing the soil, hot air, and a chemical base with a large diameter vertical auger. When using this method, an SVE system is used to capture and dispose of volatilized contaminants. This

strategy is relatively simple and can be completed in a relatively short time.

5.2.5.2 Evaluation of Groundwater Remediation Options

In TVA's view, Monitored Natural Attenuation is the preferred option because there is strong evidence that the CNS components are degrading and because it will be difficult, if not impossible, to treat those components lodged in the bedrock's pore space in a reasonable timeframe. However, TVA also believes it would be appropriate to better quantify the amount of CNS-derived contamination likely to reach the surface before this option is implemented.

Should the use of Monitored Natural Attenuation be deemed unacceptable by the parties involved, then the *ex-situ* groundwater pump and treat option, as proposed by TransTechnology Corporation is likely the only other practical alternative. However, to accurately place the extraction wells, it is recommended the contaminant plume be better delineated since a recent characterization of the groundwater indicates that the contaminant plume may have a more southerly component than previously predicted. It is recommended that this option be coupled with the least costly treatment system available, since the system may be operated for several decades.

5.2.6 Results of the Evaluation of Injection and Recovery Alternatives

In comparing injection and recovery scenarios, eight different delivery/recovery systems for treating soil in the landfill overburden were evaluated using numerical modeling analysis.

For delivering additives to the soil, an infiltration gallery was found to be superior to shallow injection wells because it allowed higher influx rates and provided better distribution of additive in the soil. Modeling with the infiltration galleries indicates that 1.3 pore volumes per year of aqueous-based additive could be added to the soil overburden. This is an order of magnitude greater than alternatives relying on vertical wells or trench systems.

The optimal recovery system included horizontal wells installed at the base of the disposal area. Model predictions indicated that over 80% of the additive introduced in the infiltration gallery will be extracted by the horizontal wells. This was higher than alternatives involving

trenches or vertical wells.

5.3 Summary

The following conclusions were drawn regarding the fate and effect of CNS tear gas components.

- All three CNS tear gas components are DNAPLS and, in vapor phase, are much heavier than air.
- Chloroform and chloropicrin have similar soil sorption coefficients that are about half as high as the sorption coefficient for phenacyl chloride.
- Chloroform is the most recalcitrant of the three CNS components and has been detected in the highest concentrations in groundwater down-gradient of the landfill.
- Microcosm degradation studies have revealed that chloropicrin and phenacyl chloride have aerobic degradation half-lives of a few days. Chloropicrin's half-life may be shorter than a day.
- Chloroform's aerobic degradation half-life is in the order of 200 to 300 days.
- Both chloropicrin and phenacyl chloride are fairly reactive and are not expected to impact surface water quality down-gradient of the site.
- There is strong evidence that the CNS components are being degraded at Area 15A.
- Both chloroform and chloropicrin can be analyzed using Direct Sampling Ion Trap Mass Spectrometry. Phenacyl chloride is unsuitable for quantitative analysis by DSITMS due to its low volatility and interaction with water.

Conclusions regarding the fate and transport of CNS tear gas contaminants in groundwater are as follows:

- Groundwater flow beneath the tear gas landfill is typical of fractured media in which groundwater flows preferentially through a few hydraulically active fractures with only minor flow through the porous rock matrix.
- Among the degradation half-lives used in model simulations, a degradation half-life for chloroform of 277 days yielded groundwater and seep concentrations that were in best agreement with that observed at the site.

- Chloroform levels at the site have already peaked and improving conditions should continue in the future.
- By the year 2000, all of the tear gas material originally buried should no longer reside in the original containers (based on the observation made in 1985 that 90% of the original tear gas was no longer in drums).
- Complete removal of the tear gas remaining in the soil overburden by the year 2000 will not significantly reduce the time required for natural restoration of the bedrock aquifer.
- Concentrations at the discharge boundary (the seeps) should fall below the MCL of 10^{-4} g/L by the year 2010.
- Based on the 277-day half-life, chloroform stored in bedrock matrix should be depleted by the year 2050

Conclusions that can be drawn from the simulation of delivery and recovery systems are as follows:

- Delivery of additives to the pore space of the soil overburden is limited by the low permeability of the soil.
- An infiltration gallery or aboveground irrigation system is the preferred means for delivering additives to the soil matrix.
- Horizontal extraction wells placed at the soil/bedrock interface would provide the most efficient recovery of groundwater and additive. Over 80% of the applied additive would be recovered.
- The optimal system would provide 1.3 soil volumes per year of aqueous-based additive to the landfill overburden.

The conclusions from the evaluation of remedial strategy alternatives are as follows:

- There has been no field work involving the remediation of CNS tear gas contaminants.
- Chloroform is one of the more difficult chlorinated solvents to oxidize.
- The soil in the tear gas landfill has a lower pH than surrounding soil due to the presence of hydrochloric acid produced from the degradation of the CNS components.
- A chemical/biological (abiotic/biotic) approach is the preferred method for remediating the soil in the tear gas landfill area. Ammonium hydroxide is the preferred base.

Methanol would be added to stimulate the growth of soil methylotrophs that can rapidly break down chloroform.

- An alternative treatment method for the soil involves *in-situ* addition of hot air using a large diameter mixing auger. A base could be added along with hot air if treatability studies show that it is worthwhile. Vapor extraction may be required to capture and treat gaseous emissions.
- For treating groundwater, Monitored Natural Attenuation is the recommended strategy. This is supported by the strong evidence that degradation of CNS compounds is occurring and the fact that fractured media are unsuitable for pump and treat technologies.
- Plume containment, as being proposed by the site owner, is the second alternative for mitigating CNS contamination problems.
- A better delineation of the contaminant plume as well as a better quantification of the amount of CNS derived contaminants that are reaching the surface via seeps is needed to design and support either groundwater remedial strategy.

5.4 Recommendations for Future Research

Recommendations regarding future research with CNS tear gas contaminants should be based on the military's needs. Relative to other organic contaminants and metals, CNS tear gas contamination is not widespread. Specific research needs derived from this study concern Area 15A. Appendix H (Evaluation of Injection and Recovery Alternatives) provides a detailed list of information that could be useful for developing a better understanding of the groundwater flow system at Area 15A and for selecting and designing a remedial strategy. If consideration is given to remediating the source area, the following field studies are recommended:

- Sampling and analysis of the landfill soil to determine the hydraulic and physical properties.
- Installation of shallow piezometers within the drum disposal area to verify the presence of perched groundwater conditions and to provide some impression of transient wetting from precipitation events.

- A geophysical survey of the landfill to determine the dimensions and interconnectivity of drum voids. This has important implication regarding the design of an injection/recovery system.

To assess the environmental risk of offsite migration of contaminants and to support a natural attenuation strategy, the following field studies should be conducted:

- Identification and continuous monitoring of seeps before, during, and after precipitation events to provide temporal characterization of contaminant concentrations.
- Continuous flow and water quality monitoring of Tributary B of Elders Run before, during, and after precipitation events to provide temporal characterization of contaminant concentrations and to develop accurate water balance estimates.

SECTION 6.0

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APPENDIX A

SOIL AND GROUNDWATER SAMPLE COLLECTION PLAN

SAMPLE COLLECTION PLAN

and

HYDROGEOLOGIC DATA COLLECTION PLAN

for

AREA 15A

at the

FEDERAL LABORATORIES FACILITY

SALTSBURG, PENNSYLVANIA

Prepared for the

U.S. ARMY ENVIRONMENTAL CENTER

Aberdeen Proving Ground, Maryland

Prepared by

Tennessee Valley Authority

Environmental Research Center

Muscle Shoals, Alabama

November 1997

TVA Contract No. TV-99802V

MIPRA596

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1. INTRODUCTION

The U.S. Army is interested in determining the fate of CNS tear gas buried in soil. Although the Department of Defense (DoD) has sites where CNS tear gas contamination may be present, little data are available on the fate of tear gas in soil or on the environmental processes which affect CNS tear gas as it moves through soil. To address this problem, the United States Army Environmental Center (USAEC) contracted with Tennessee Valley Authority Resource Management (TVA RM) to conduct a scientific study of the TGFE of CNS tear gas in soils. This study is commonly referred to as the Tear Gas Fate and Effects (TGFE) study. The TGFE study will be conducted using soil and ground water samples collected from the Federal Laboratories Plant No. 3 in Saltsburg, Pennsylvania.

The objective of the TGFE study is to obtain information about the behavior of soil-borne CNS tear gas components and to determine their fate in soil. Specific information to be gathered include:

- Soil characteristics at the Saltsburg site
- CNS degradation and mineralization rates
- The degree at which CNS components are sorbed by soil
- Transport properties in the form of a soil-gas diffusion coefficient for each CNS component
- Volatility data including CNS component vapor density and Henry's Law coefficients.

This information will be used in conjunction with hydrogeologic data to a develop computer model of the flow of contaminates and ground water under the Saltsburg site. This model is referred to here as the "flow and contaminate transport model." The flow and contaminate transport model will be used to develop remediation recommendations in later stages of the TGFE project.

The TGFE project's data and sample collection plan, this document, outlines the procedures to be used to collect soil samples and field data needed to support of the TGFE study. In addition, the sample collection plan outlines the procedures to be used to collect soil and ground water samples in support of a separate methods development study being conducted by the Oak Ridge National

Laboratory (ORNL). The ORNL study is investigating the use of Direct Sampling Ion Trap Mass Spectrometry (DSITMS) to measure contaminant concentrations in soil and ground water.

The sampling and data collection plan has two main sections. Section 2.0 describes the sampling procedures to be used to collect soil and ground water samples in support of tasks to be conducted in the laboratory during the TGFE and ORNL studies. Section 3.0 describes the field data collection and collection procedures to be used to support the computer modeling effort.

The sampling plan in Section 2.0 covers two activities: (1) collecting uncontaminated and contaminated soil for use by TVA in the TGFE study and the flow and contaminant transport model and (2) collecting both contaminated and uncontaminated groundwater and soil for use at the ORNL, under contract to TVA, in developing analytical methods for the contaminants of concern.

The first sample collection activity involves collecting uncontaminated soil for the TGFE study and contaminated soil to support the flow and contaminant transport modeling. Uncontaminated soil will be collected around the perimeter of Area 15A to obtain representative soil properties for use in the TGFE study. Contaminated soil will be collected from a known contaminated area within the landfill to determine the degradation rate constant which will be used in the flow and contaminant transport model.

In addition, TVA has been requested to collect one contaminated groundwater sample, one contaminated soil sample, one uncontaminated groundwater sample, and one uncontaminated soil sample. ORNL, under contract to TVA, plans to use the contaminated and uncontaminated samples in developing DSITMS analytical methods for determining the concentration of CNS contaminants in soil and groundwater. The methods developed will potentially be used to obtain field measurements of the *contaminants in situ* using the DSITMS.

This sampling plan outlines the methods to be used for collecting the following three items:

- Uncontaminated and contaminated soil for use in the TGFE study and the flow and transport modeling,
- Contaminated and uncontaminated soil for developing DSITMS analytical methods, and

- Contaminated and uncontaminated groundwater for developing DSITMS analytical methods.

The data collection plan (Section 3.0) covers the collection of (1) site specific information such as continuous precipitation data and continuous groundwater level data, (2) *in situ* measured horizontal hydraulic conductivities, and (3) site specific samples for laboratory measurement of vertical hydraulic conductivity, porosity, and dry bulk density. The data described here will primarily support the flow and contaminant transport modeling efforts.

The sampling and data collection plans presented here are limited to describing how the sampling and data collection will be conducted. They do not include details for the TGFE study, the site specific modeling efforts, or the development of the DSITMS analytical methods.

2. SAMPLE COLLECTION PLAN

2.1 Sampling Operations

2.1.1 Overview

The purposes of the sampling operations will be (1) to obtain uncontaminated soil for use in the TGFE study, (2) to obtain contaminated soil for use in the flow and contaminant transport modeling, and (3) to obtain contaminated and uncontaminated soil and to obtain contaminated and uncontaminated groundwater for use in developing DSITMS analytical methods for CNS.

Eight samples of uncontaminated soil from three areas adjacent to the Area 15A site are to be collected for the TGFE study. A duplicate sample of uncontaminated soil from one of these eight samples will be collected for the method development. One sample of a known area of contaminated soil will be collected for the flow and contaminant transport modeling effort. Also, one sample each is to be collected from a known contaminated monitoring well, a known uncontaminated (without CNS) monitoring well, and a known area of contaminated soil for use in DSITMS methods development. The uncontaminated soil samples associated with the TGFE study will all be collected before collecting any other samples.

Table 2-1 summarizes the sample identifications, locations, collection depths, quantities, and type of container. The field data will be collected and recorded on a field log sheet. The field log sheet is shown in Table 2-2.

The TVA sampling personnel will maintain custody of the samples from the time of collection until the samples are hand-delivered to ORNL or TVA. A chain-of-custody record will be maintained as identified in TVA's Specialty Laboratory (SL) procedure SP-0001, "Sample Chain-of-Custody."

2.1.2 Uncontaminated Soil Collection (Method Development and TGFE Study)

The uncontaminated soil for the method development and the TGFE study will be collected from three locations outside the perimeter of Area 15A. The general locations of the three soil collection locations are shown in Figure 2-1. The exact three locations will be coordinated with TransTechnologynology personnel. To maintain similar soil properties to the landfill soil, the soil collection locations will not be greater than 30 feet outside the landfill perimeter.

Table 2-1

Federal Laboratories Facility, Saltsburg, Pennsylvania, Samples to be Collected

Sample Identification	Sampling Location	Sampling Depth feet	Minimum Quantity Kg (lb.)	Sample Container	Sample Preservation	Intended Use of Sample & Intended User	Sampling Location Description
Soil-1	15A-1	0-2	8 (18)	Triple Bagged	none	TGFE Study-TVA	outside NW corner of Landfill
Soil-1A	15A-1	0-2	8 (18)	Triple Bagged	none	Methods Development - ORNL	outside NW corner of Landfill
Soil-2	15A-1	2-4	14 (31)	Triple Bagged	none	TGFE Study-TVA	outside NW corner of Landfill
Soil-3	15A-2	0-2	8 (18)	Triple Bagged	none	TGFE Study-TVA	outside SW corner of Landfill
Soil-4	15A-2	2-4	14 (31)	Triple Bagged	none	TGFE Study-TVA	outside SW corner of Landfill
Soil-5	15A-2	4-6	8 (18)	Triple Bagged	none	TGFE Study-TVA	outside SW corner of Landfill
Soil-6	15A-3	0-3	8 (18)	Triple Bagged	none	TGFE Study-TVA	outside SE corner of Landfill
Soil-7	15A-3	3-6	8 (18)	Triple Bagged	none	TGFE Study-TVA	outside SE corner of Landfill
Soil-8	15A-3	6-8	8 (18)	Triple Bagged	none	TGFE Study-TVA	outside SE corner of Landfill
Soil-9	Contaminated Soil identified by TransTechnology	<10 feet as identified by TransTechnology /AEC	3.6 (8)	Teflon™ lined core (2)	cool on ice	Methods development-ORNL	area of known contaminated soils to be determined by TransTechnology
Soil-10	same as Soil-9	same as Soil-9	4 (9)	Plastic line core (2+)	cool on ice	Modeling	same as Soil-9
Groundwater-1	Uncontaminated monitoring well identified by TransTechnology	Water Surface	4 liters 6-40 ml vials	1-L NM Amber Glass 6-40 ml vials	pH < 2 cool on ice	Methods development-ORNL	Uncontaminated monitoring well identified by TransTechnology
Groundwater-2	Contaminated monitoring well identified by TransTechnology	Water Surface	4 liters 6-40 ml vials	1-L NM Amber Glass 6-40 ml vials	pH < 2 cool on ice	Methods development-ORNL	Contaminated monitoring well identified by TransTechnology

Notes:
Sample locations Soil 1 - Soil 8 should be outside the Area 15A landfill perimeter, but not more than 30 feet away.
Larger soil quantities are needed in some cases to account for coarse material (gravels, etc.).
AEC or TransTechnology personnel will identify all sample locations.
The groundwater samples should be preserved with concentrated hydrochloric acid.

Table 2-2

Federal Laboratories Facility, Saltsburg, Pennsylvania, Field Log

Sample Identification	Sampling Date 1997	Sampling Time EST	Sampling Depth (feet)	Odor Detected (Y/N)	Description of Sample	Other Observations
Soil-1						
Soil-1A						
Soil-2						
Soil-3						
Soil-4						
Soil-5						
Soil-6						
Soil-7						
Soil-8						
Soil-9						
Soil-10						
Groundwater-1						
Groundwater-2						

Notes:

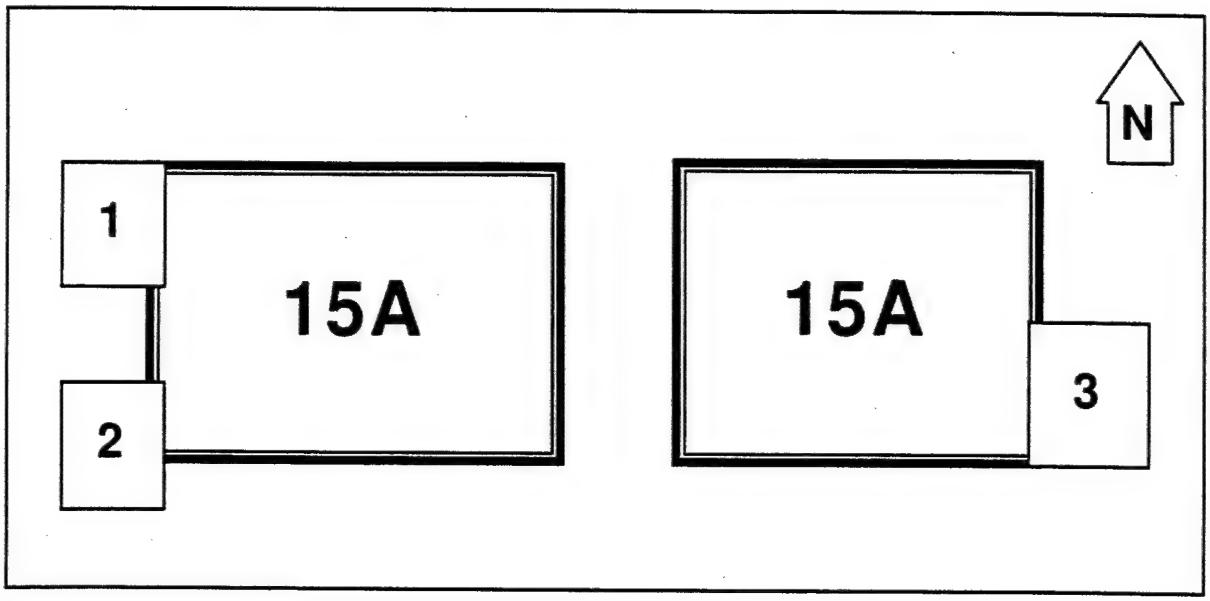


Figure 2-1

General Locations For Uncontaminated Soil Collection

Eight specimens of uncontaminated soil will be collected from the three designated areas adjacent to the Area 15A site for the TGFE study. In addition, one duplicate sample, Soil-1A, will be collected along with the eight specimens for use in method development. Table 2-1 summarizes the sample identifications, locations, collection depths, quantities, and type of container. A field log sheet will be kept during the soil collection. The field log sheet is shown in Table 2-2.

The soil collection will initiate in the most upgradient location and proceed in the downgradient direction. Prior to soil collection at each location, the leaf and plant litter will be cleared away. Samples at each location will be collected at the depths shown in Table 2-1. Fiberglass post-hole diggers will be used to collect the soil samples at depths of 0 to 2 feet. At sampling depths below 2 feet, a Little Beaver Earth Drill® with 6-inch flight metal augers will be used. Once the desired depth is reached with the drill, the augers will be removed and a hollow stainless steel bucket auger with a T-handle and extensions will be inserted to retrieve the soil. Multiple bucket auger volumes will be required to obtain the necessary quantity of soil.

The soil collected will be placed directly into a labeled plastic bag (see Table 2-1 for the label identifications). The soil collected will be triple bagged in large heavy duty plastic bags and placed in containers for transfer (e.g., cardboard boxes) to ORNL in Oak Ridge, Tennessee, and to TVA in Muscle Shoals, Alabama. The soil is not to be preserved in any way. The soil will be transported by the TVA sampling personnel.

The extra uncontaminated soil removed from each boring will be placed back in the boring from which it originated when the soil collection is complete. Any removed contaminated soil, as determined by sight or smell, will be placed in a 55-gallon open-top metal drum and disposed by TransTechnology.

2.1.3 Contaminated Soil Collection (Modeling)

Contaminated soil for microbiological mineralization studies will be collected with a Geoprobe® Macro-Core Sampler using clear plastic liners made of polyethylene terephthalate (PETG). The sampling device and liner will be sterilized with ethanol and allowed to air dry prior to sample collection. The sample will be collected from soil that is both contaminated and beneath the groundwater table. See Figure 2-2 and Figure 2-3 to identify the approximate sampling location. It is anticipated that the sampling depth will be approximately 9 feet. After the sample has been

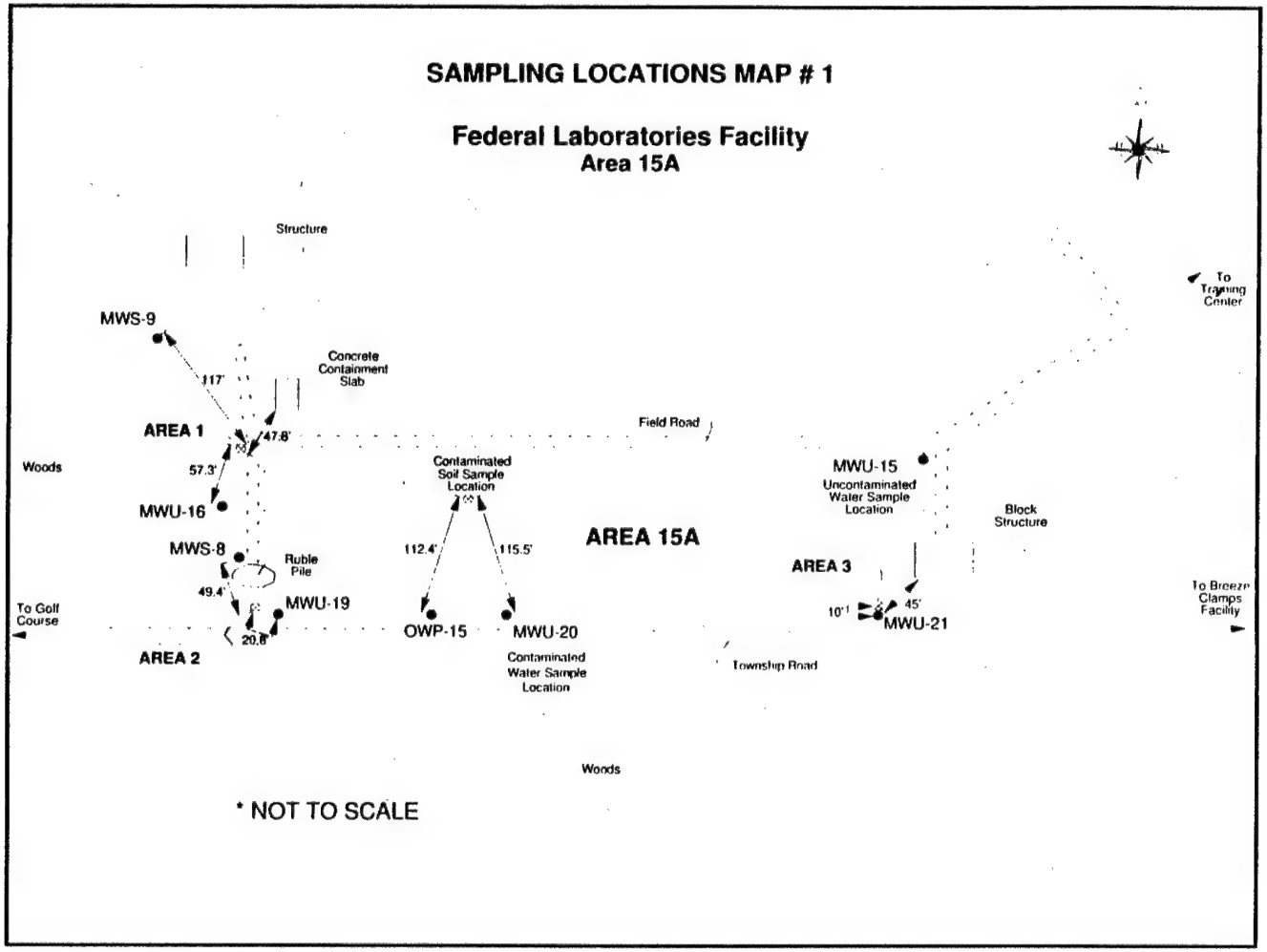
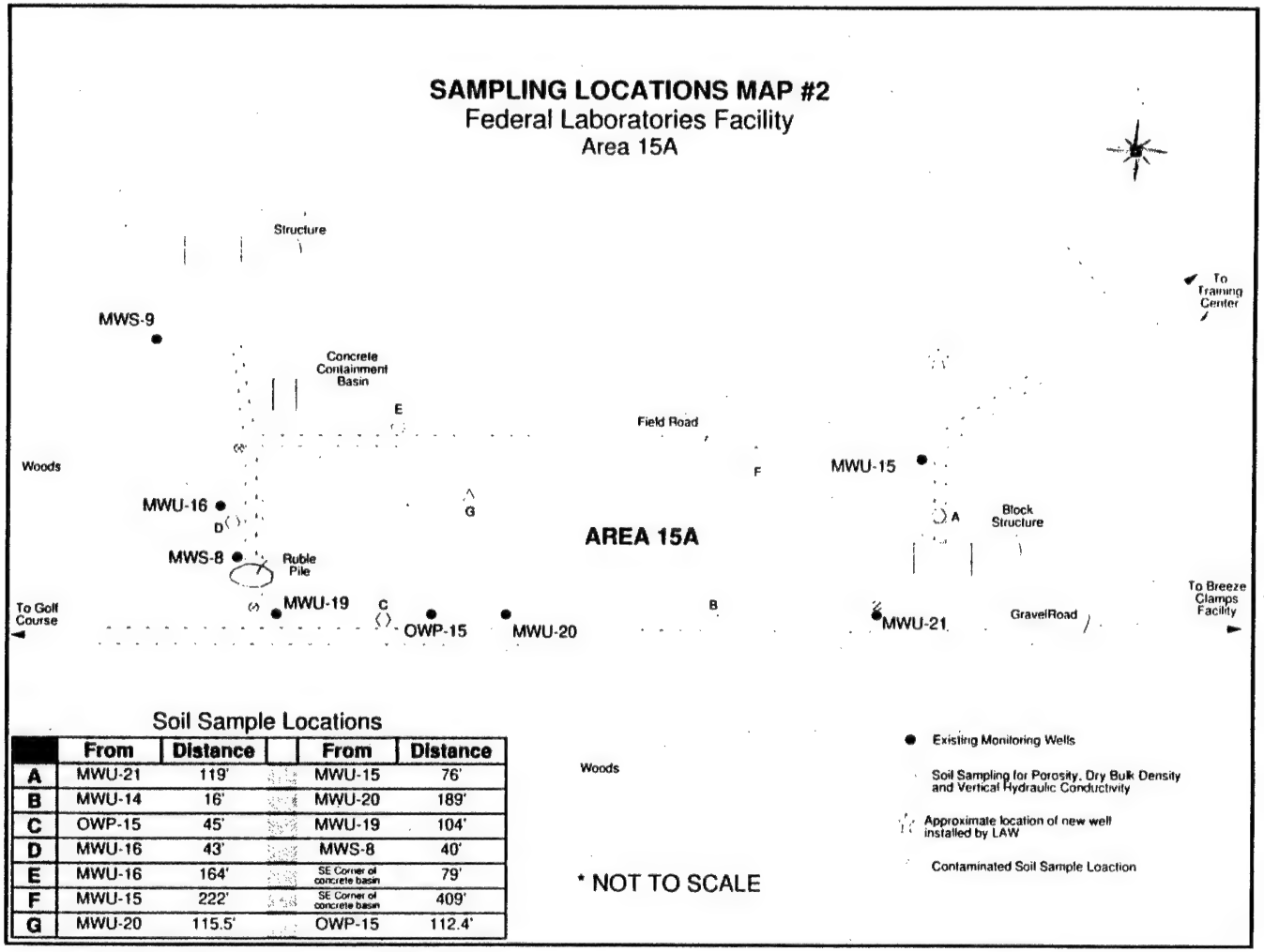


Figure 2-2

Sampling Locations Map #1



	From	Distance		From	Distance
A	MWU-21	119'		MWU-15	76'
B	MWU-14	16'		MWU-20	189'
C	OWP-15	45'		MWU-19	104'
D	MWU-16	43'		MWS-8	40'
E	MWU-16	164'		SE Corner of concrete basin	79'
F	MWU-15	222'		SE Corner of concrete basin	409'
G	MWU-20	115.5'		OWP-15	112.4'

Figure 2-3

Sampling Locations Map #2

retrieved from the ground, it will immediately be prepared by: (1) cutting the top 6 inches and bottom 2 inches off, then (2) both ends of the liner will be covered with Teflon® tape and sealed with friction fit vinyl end caps (black denotes bottom of sample, orange denotes the top), and finally (3) placed in an ice chest with a layer of cardboard separating the sample from ice to prevent sample from freezing. Latex gloves will be worn at all times when handling the samples. If necessary, multiple soil cores will be collected to provide sufficient sample volume for testing. See Table 2-1 for identification and preservation information. The contaminated soil sample will be delivered to TVA in Muscle Shoals within 72 hours of sample collection and refrigerated at 4°C until tested.

2.1.4 Contaminated Soil Collection (Method Development)

One specimen of contaminated soil for analytical method development will be collected from a location and depth (<10 feet deep) identified by TransTechnology personnel. Table 2-1 summarizes the sample information.

One 3.6 kg (8 lb) soil sample will be obtained. The sampling depth will be reached by either fiberglass post-hole diggers (0-2 feet depth) or a Little Beaver Earth Drill® (for a sample > 2 feet deep) as described in Section 2.1.2. Once the depth of the boring reaches to within six inches of the desired sampling depth, the motorized mechanical augers or post-hole diggers will be removed from the boring. To reduce volatilization of contaminants, hand-held stainless steel bucket augers will be used to remove the remaining six inches of soil. Once the top of the sampling interval is reached, the bucket auger will be removed and a Geoprobe® Macro-Core Sampler with Teflon® liner will be inserted into the boring and pushed approximately 40 inches deeper. The sampler will then be removed from the boring and the Teflon® liner removed. The sample will be immediately prepared by cutting the top 6 inches and the bottom 2 inches off. Teflon® tape (3 mil thickness) will be used to cover the exposed ends of the sample before "friction fit tight" vinyl end caps are placed on the ends of the sample core. The process will be repeated in the same boring and at the same depth in order to collect sufficient volume.

No chemical preservatives will be added. The two sample cores will be immediately placed on ice in an ice chest. The ice will be bagged to prevent melting ice from contacting the sample containers. To maintain the cooled status of the soil samples until the sample cores are delivered to the laboratory, the bagged ice will be checked periodically and replaced as necessary. The samples will be delivered to ORNL in Oak Ridge, Tennessee, by the TVA sampling personnel.

The extra soil removed from the boring at the contaminated soil location will be placed in a 55-gallon open-top drum and disposed by TransTechnology. The boring will be filled with a cement and bentonite grout mixture as defined in ASTM D5299, "Standard Guide for Decommissioning of Groundwater Wells, Vadose Zone Monitoring Devices, Boreholes, and Other Devices for Environmental Activities."

2.1.5 Contaminated and Uncontaminated Groundwater Collection (Method Development)

One sample each of contaminated and uncontaminated groundwater for analytical method development will be collected. The monitoring wells TransTechnology identified for sampling are well number MWU-20 (contaminated) and well number MWU-15 (uncontaminated).

The contaminated and uncontaminated groundwater samples will be collected after two well volumes have been purged from each respective well. Each well will be purged using a disposable Teflon® bailer. The purge water will be contained in a 55-gallon bung-type drum. The sampling will be conducted in accordance with the requirements of Chapter 4, Organic Analyses, of the Environmental Protection Agency (EPA) publication, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) and ASTM D4448, "Sampling Groundwater Monitoring Wells."* The contaminated sample will be collected from the bottom of the respective well's screened interval with a Teflon® double check valve bailer. The uncontaminated sample will be collected from just below the water's surface of the respective well with a disposable Teflon® single check valve bailer.

The contaminated and uncontaminated groundwater samples will be collected in the appropriate containers for both volatile organic analyses and semivolatile organic analyses. Both samples will be collected in four 1-liter amber narrow-mouth glass bottles with Teflon™-lined caps and six 40 milliliter glass vials with Teflon®-lined septa. The samples collected for volatile organic analyses will be preserved onsite with 1:1 HCL to a pH of less than 2. A calibrated pH meter will be used to determine the quantity of 1:1 HCL required to lower a 40 milliliter aliquot of the sample to a pH of less than 2. This quantity will then be added to each vial before it is filled with the sample. The 1 liter containers for semivolatile organic analyses will not be preserved with acid.

To obtain the groundwater samples, Teflon® bailers with nylon cords will be lowered slowly down to the desired location in each well. After the bailer is filled, it will be gently lifted to the ground surface where it will be immediately placed in preserved sample containers. The sample containers will be filled by slowly and gently by dispensing the water from the bailer to the container. The

water will be mixed and agitated as little as possible to prevent volatilization of volatile organic compounds. Each container will be filled completely leaving no headspace or air pockets. Spillage will be contained in a stainless steel pan which will be poured into a 55-gallon bung-type metal drum after the sampling is complete and will be disposed by TransTechnology.

The sample containers will be immediately placed on ice in an ice chest. The ice will be replaced and the water drained as necessary until the sample containers are delivered to the laboratory. The samples will be delivered to ORNL in Oak Ridge, Tennessee, by the TVA sampling personnel.

2.1.6 Sample Identification

The samples will be labeled with the sample identifications listed in Table 2-1. In addition, the date of sampling and the words "Federal Laboratories - Area 15A" will also be written on the label. The preparation of the labels will be done in advance of the sampling to reduce chances of contamination from the marker. An example of a label is shown below.

Soil-10

11-19-97

Federal Laboratories - Area 15A

2.1.7 Sample Location Identification

Each soil collection location will be referenced by distance to two or more benchmarks such as a building corner, a corner fence post, a telephone pole, or a similar object. The distances will be physically measured with a tape. A drawing of the sample locations will be produced showing the relative positions of the benchmarks, the sampling locations, and the landfill perimeter. The locations of the monitoring wells have been documented in previous groundwater monitoring reports for the site.

2.2 EQUIPMENT WASHING AND DECONTAMINATION

Before being transported to the site, all sampling equipment will be washed with tap water and Liquinox detergent. After each piece of equipment is washed, it will be rinsed with tap water and then lightly sprayed with isopropyl alcohol and allowed to air dry.

TransTechnology will furnish and transport the four drums to the sampling site for the investigative derived waste. This includes furnishing (1) two bung-type 55-gallon drums near the monitoring wells to be sampled, (2) one open-top drum near the contaminated soil location, and (3) one open-top drum in the general vicinity of Area 15A for disposal of Tyvek suits, booties, etc.

All Tyvek suits, rubber booties, gloves, paper towels, wipe cloths, respirator cartridges, bailers/cord, and other miscellaneous disposable items will be placed in a 55-gallon open top metal drum supplied by TransTechnology.

TransTechnology will handle the disposal of all the investigative derived waste.

2.2.1 Uncontaminated Soil Collection

After each soil sample collection, the equipment used will be cleaned of soil residues with tap water, Liquinox detergent, and wire brushes. The rinsate will be allowed to fall directly to the ground adjacent to each boring. If contamination is suspected as evidenced by sight or smell, then the rinsate will be contained in a drum and isopropyl alcohol will be used in each cleaning process.

After completing the collection of the uncontaminated soil samples, all the used equipment will be washed with tap water and Liquinox detergent, then rinsed with tap water and sprayed with isopropyl alcohol. The equipment will be allowed to air dry before being used again.

2.2.2 Contaminated Soil Collection

After collection of the soil, the used equipment will be cleaned of soil residues with tap water, Liquinox detergent, wire brushes, and isopropyl alcohol. The rinsate will be collected in a stainless-steel pan and transferred to a 55-gallon drum. The stainless-steel pan will also be cleaned as described above and the rinsate placed in the drum.

All tap water, Liquinox detergent, and isopropyl alcohol used in washing and decontaminating the augers and equipment from the contaminated soil sample collection will be placed in the same drum as described above.

All the soil from the boring where the contaminated soil sample is collected will be placed in a 55-gallon open-top metal drum furnished by TransTechnology.

2.2.3 Contaminated and Uncontaminated Groundwater Collection

New disposable Teflon® bailers will be used for the collection of the groundwater samples. Each bailer will be left in its protective wrapper until just prior to use. No washing or decontamination will be necessary. The bailers will be discarded after use in an open-top 55-gallon drum along with the Tyvek suits, rubber booties, gloves, paper towels, wipe cloths, respirator cartridges, cord, and other miscellaneous disposable items.

All water spillage from the contaminated groundwater sampling will be contained in a stainless steel pan until the sampling is completed. The contaminated groundwater will be transferred to a 55-gallon bung-type metal drum furnished by TransTechnology. The stainless steel pan will be washed with tap water and Liquinox detergent and then rinsed with isopropyl alcohol. The tap water, Liquinox detergent, and isopropyl alcohol used will be transferred to the same drum. Also, the purge water from the contaminated and uncontaminated monitoring wells will be placed in a 55-gallon bung-type metal drum.

3. HYDROGEOLOGIC DATA COLLECTION PLAN

3.1 DATA COLLECTION OPERATIONS

3.1.1 Overview

In order to collect site specific data needed for the flow and contaminate transport model, TVA will need various types of continuous data over an extended period in order to evaluate physical relationships at the site. Also, TVA needs to conduct *in situ* testing and sampling to determine hydrogeologic characteristics of the site.

3.1.2 Groundwater Levels

Continuous groundwater level data will be recorded up to six months for selected wells. The wells to be monitored are monitoring wells MWU-15, MWU-19, MWU-20, and OWP-15. A Telog® data logger and Druck® pressure transducer (or equivalent equipment) will be installed and adjusted to record relative groundwater elevations for each respective well. The accuracy of the data logger and pressure transducer will be checked for the range of anticipated groundwater fluctuation. The accuracy of the equipment will be checked at installation, at removal, and at a specified interval. The data logger will be clamped to the outside of the well casing.

Data will be retrieved onsite with a portable laptop computer. The data will be stored electronically on a floppy disk and on the computer's internal hard drive. Hard copies of the data will be generated when the data disk and computer arrive back at TVA offices.

3.1.3 Precipitation

A tipping-bucket type rain gage will be installed at the site to record the frequency, intensity, and duration of precipitation events

The rain gage will be installed to continuously monitor precipitation for a period up to six months. It will be installed in an open location away from trees, buildings, and other potential interference in accordance with USGS procedures. Also, a location will be sought where the gage will be least likely to be vandalized.

Data will be retrieved onsite periodically with a portable laptop computer. The data will be stored electronically on a floppy disk and on the computer's internal hard drive. Hard copies of the data will be generated when the data disk and computer arrive back at TVA offices.

3.1.4 Soil and Bedrock Hydraulic Conductivity

Additional hydraulic conductivity data are needed for overburden soils, the Saltsburg and Buffalo sandstone units, and intervening shale aquitards. The only data currently available are average hydraulic conductivity estimates for the Saltsburg sandstone based on pumping tests conducted at wells MWS-8, MWU-14, and MWU-20. Both field and laboratory methods are proposed for obtaining the additional data.

Borehole flowmeter testing of six existing wells is proposed to obtain discrete estimates for the horizontal component of hydraulic conductivity (K_h) for the soil, Saltsburg, Buffalo, and shale aquitards. Tests will involve stressing each well at a constant rate (either by pumping or injecting water) while measurements of borehole water velocity are measured at 0.5 ft intervals over the full length of the well screen. Tests will provide discrete estimates of K_h for each formation. Well flow profiles will also be used to determine the relative importance of bedrock fracture and matrix flows.

Since all of the existing wells are only screened over 10 to 15 ft intervals, one new test well screened over the full thickness of the Saltsburg sandstone will be constructed to obtain a complete flow and K_h profile for the aquifer. This well will be located north and east of the disposal area as shown approximately on Figure 2-3.

Estimates of the vertical hydraulic conductivity (K_v) of the soil will be obtained by laboratory testing of six soil cores collected in the immediate vicinity of the disposal site. The approximate locations of the six sample locations are shown on Figure 2-2. Minimally disturbed soil samples will be collected in 1.5-inch diameter plastic liner tubes using a Geoprobe® sampler. ASTM method D2434-68 will be used to estimate K_v for each sample.

3.1.5 Soil Porosity and Bulk Density

Measurements of porosity and dry bulk density will be performed on six soil cores collected in the immediate vicinity of the disposal site. The sampling locations will be the same as those for the soil hydraulic conductivity as shown on Figure 2-2. Also, the method of soil sampling will be the same as that described in section 2.1.3. Laboratory method MOSA Chapter 18 will be applied in porosity measurements, and ASTM D2937 will used to obtain density estimates.

4. HEALTH AND SAFETY PLAN

The Site Specific Health and Safety Plan addresses personal protective equipment, emergency procedures, subsurface drilling authorization, and various other health and safety concerns. The plan is included as Appendix A-1.

APPENDIX A-1

SITE-SPECIFIC HEALTH AND SAFETY PLAN FOR COLLECTING SOIL AND GROUNDWATER SAMPLES FROM AREA 15A OF THE TRANSTECHNOLOGY CORPORATION FACILITY SALTSBURG, PENNSYLVANIA

PREPARED BY LYNN HOLT, Dr. P.H.

January 1997

(Revised March 1997)

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1.0 GENERAL

The Site-Specific Health and Safety Plan is designed to ensure the health and safety of Tennessee Valley Authority (TVA) personnel performing work on Area 15A at the TransTechnology Corporation site in Saltsburg, Pennsylvania. This plan will be used in conjunction with the "Sample Collection Plan for Soil and Groundwater near Area 15A at the Federal Laboratories Facility, Saltsburg, Pennsylvania," dated January 1997. All activities associated with this work will be in compliance with this health and safety plan, the Occupational Safety and Health Administration standards including 29 CFR 1910.120, and the TVA Safety Manual. Guidance references for specific operations are included in TVA Occupational Health and Safety Manual and TVA Hazard Control Manual.

Many different types of pyrotechnical products have been manufactured at the TransTechnology Corporation facility, principally smoke generators using chloroacetophenone (CN) and o-chlorobenzylidene (CS). These compounds have distinctively irritating odors (See Table 1 below) recognizable at relatively low concentrations enabling them to be readily detected.

Table 1 Chemical Characteristics

Chemical	CAS Number	PEL/TLV	IDLH	Odor Threshold	Odor Description
CN	532-27-4	0.3 mg/m3	15 mg/m3	0.1 mg/m3	Sharp, Irritating
CS	2698-41-1	0.4 mg/m3	2 mg/m3	Not Available	Pepper-like
Chloropicrin	76-02-2	0.7 mg/m3	14 mg/m3	7.5 mg/m3	Intensely irritating
Chloroform	67-66-3	10 mg/m3	2480 mg/m3	1000 mg/m3	Pleasant, Sweet

In the late 1940s, it is suspected that an estimated 300 to 1,700 barrels of CNS (CN and chloropicrin in chloroform) were buried in Area 15A. Tear gas grenades and projectiles, smoke grenades and projectiles, and flares were once produced at the facility.

The collection activities at the sites are for two purposes (1) to collect uncontaminated and contaminated soil for use by TVA in a fate and effects study, and (2) to collect both contaminated and uncontaminated groundwater and soil for use by the Oak Ridge National Laboratory in developing analytical methods for the contaminants of concern.

Uncontaminated soil samples will be collected from three sites just outside the perimeter of the drum burial areas of Area 15A. Site personnel will identify sample locations near, but not

over, buried drums or utility lines. Using manual post-hole diggers, soil will be collected from two sites at various depths extending down to two feet. Soil will be collected then at depths down to six or eight feet using a Little Beaver® Hydraulic Earth Drill. (Noise level measures made during the operation of the Little Beaver® at the operators ear were 73 dBA while idling and 83 dBA at full throttle which indicates no hearing protection is required.) After sampling, the excavated holes will be refilled.

In addition to the uncontaminated soil samples, TVA will collect one contaminated soil sample. The contaminated soil sample will be collected from a location and depth (<8 feet deep) to be identified by TransTechnology personnel. The soil sample will be obtained by using either fiberglass post-hole diggers (0 - 2 feet depth) or a Little Beaver® Hydraulic Earth Drill (for a sample > 2 feet deep).

One sample of contaminated (with CNS components) groundwater and one sample of uncontaminated groundwater will be collected from groundwater monitoring wells selected by TransTechnology personnel. The uncontaminated well will be hydrogeologically upgradient of the Area 15A site and free of CNS components. Based on previous well analytical data from the wells surrounding Area 15A, highest levels of contamination for chloroform and chloroacetophenone were 680,000 µg/L and 36,000 µg/L, respectively. Chloropicrin was not detected in the most recent sampling.

The primary concern with this site is to protect employees if CNS chemicals are encountered during the sampling. Although the chemicals of concern are tear gas agents and should have sufficient warning properties, full-face air purifying respiratory protection will be required during the collection of the contaminated soil and groundwater sample. Respiratory protection will not be required for the other sample work until any odors such as irritating or pepper-like odors or sweet/pleasant odors or any chemical odors are noticed. Should any chemical odors be encountered, full-face respirators should be donned before work can continue. If odors penetrate the respirator, then the sample site should be abandoned until air-supplied respirators can be obtained. A wind indicator, e.g., windsock or streamer, will be installed near the soil sampling to indicate an upwind evacuation direction should it become necessary. If evacuation is necessary and symptoms warrant, medical attention should be sought.

1.1 Responsible Personnel

Onsite team leader: James C. Adams 205/386-3655

Project team leader: Michael F. Broder 205/386-2475

Project health and safety officer: G. Lynn Holt 410/612-7637

USAEC contact: A. J. Walker 410/612-6863

USAEC industrial hygiene point of contact: William P. Houser 410/612-6869

TransTechnology Corporation contact: Jeff Forgang 908/903-1600

1.2 Availability of Plan

This health and safety plan will be maintained by personnel at the site. The plan will be available to personnel involved with this site work and to federal, state, or local agencies with regulatory authority over the site.

1.3 Implementation of Plan

This plan will be reviewed by the onsite team leader with all personnel assigned to work on this site.

Documentation of all such reviews will be provided to the project team leader. The documentation will include, at a minimum, the following information:

- Date of review
- Names and signatures of those in attendance indicating that "I have read, understood, and will adhere to the requirements of this Health and Safety Plan."
- Social security number of those in attendance
- Organization of those in attendance
- Name(s) and signature(s) of those conducting the reviews

2.0 HEALTH AND SAFETY RISKS

The principal health and safety risks identified in this project involve the inadvertent release of excessive CNS buried at the site or contact with soil contaminated with CNS. Material Safety

Data Sheets for CN. chloroform. and chloropicrin are included in Attachment 1 and shall be reviewed by sampling personnel before sampling begins.

Sanitary facilities shall be made available to TVA employees by TransTechnology Corporation.

Eating. smoking. and the chewing of tobacco products on the sample site are prohibited.

Communications with emergency assistance providers shall be available onsite. Two-way radios with one radio left with TransTechnology Corporation personnel and one with the TVA team leader shall meet this requirement. TransTechnology will relay messages to emergency assistance providers. if needed. but they will not respond themselves. A cellular phone will also be available for emergency use. if possible at this site.

It is important to have the sample sites identified by TransTechnology Corporation personnel. The areas should be identified and marked before sampling begins.

An excavation permit must be completed by TVA's onsite team leader before digging or drilling begins. The permit will require an evaluation of the presence of underground utilities. As an added precaution, the use of electrical isolation gloves tested to 1 kV. should be an available option.

Weather conditions on the sample site may vary considerably; therefore, precautions may be required to prevent hypothermia or cold-related injuries. If a vehicle is used as a temporary shelter or as a warming and break area, the exhaust system should be inspected beforehand for leaks. Refer to TVA Occupational Safety Manual Bulletin: Hypothermia, The Unexpected Killer.

Site workers shall be reminded to keep all clothing and gloves away from the operating auger to ensure they are not caught and drawn into rotating equipment.

3.0 EMPLOYEE TRAINING

All employees working on the site will receive training in at least the minimum requirements listed in this section before that employee is allowed to perform any onsite work. Site workers will receive training as required in 29 CFR 1910.120 including a minimum of 40 hours of instruction off-site and a minimum of three days actual field experience under the direct supervision of a trained, experienced supervisor before being allowed to begin routine work without the direct oversight of the field supervisor. See TVA Health and Safety Manual: TVA Health and Safety Training Curriculum.

All TVA employees, including managers and supervisors, will receive a minimum of eight hours of refresher training annually.

Documentation of required training will be available onsite for inspection.

4.0 PERSONAL PROTECTIVE EQUIPMENT (PPE)

Engineering controls, work practices, PPE, or a combination of these will be used to protect employees from exposure to hazardous substances and health and safety hazards. PPE limitations must be taken into account for proper personnel safety to be maintained.

4.1 PPE Selection, Use, and Limitations

PPE will be selected and used that will protect employees from the hazards and potential hazards they are likely to encounter at the site. The selection and use of PPE will comply with 29 CFR 1910.132 through 1910.140, Personal Protective Equipment (OSHA), and with applicable manufacturer's recommendations. See TVA Occupational Health and Safety Manual, Cleaning and Disinfecting Respiratory Protection Equipment and Rescue Breathing Equipment.

As a minimum, all personnel working on sample site 15A will wear easily cleaned safety shoes (such as rubber boots), effective barrier gloves (butly rubber, Neoprene, or Viton are acceptable) when contact with soil or sediment is likely, and disposable coveralls. Hard hat and safety glasses equipped with side shields or chemical splash goggles are also required. Full-face respirators with organic vapor/acid gas cartridges (MSA GMA-H type) will be carried or easily accessible to don and use while sampling or to exit the area should any unusual odors be noticed.

5.0 MEDICAL SURVEILLANCE

As required by 29 CFR 1910.120 (f)(3)(B), all TVA employees whose duties require them to work on hazardous waste sites participate in an annual medical surveillance program. Based on anticipated exposures, additional medical surveillance will not be required unless employees become ill, or develop signs or symptoms due to possible overexposure involving hazardous substances. Documentation of satisfactory completion of the medical surveillance program will be available onsite for inspection. Refer to TVA Hazard Control Manual, Volume II, Occupational Medicine Requirements.

6.0 PERSONNEL AND AREA MONITORING

Time onsite to complete sample collection is expected to be one day. During that time, the likelihood of encountering CNS chemicals exceeding exposure limits is low as suggested by comments of previous site contractors involved in actions much more likely to encounter CNS chemicals. Should CNS chemicals be encountered during the collection of contaminated samples, employees will be protected since respiratory protection will be required. In addition, the tear gas agents are primarily acute rather than chronic hazards. Based on the low potential of worker's anticipated exposures, and the required respiratory protection, personnel monitoring will not be required.

7.0 DECONTAMINATION

Gloves, boots, and sampling equipment will be cleaned onsite in the designated decontamination area and coveralls will be removed and bagged for disposal before leaving Area 15A. Soap (Liquinox) and water will be available or accessible for decontamination of personnel. In case of skin contact with contaminated soil or liquid, the soiled area will be cleaned with soap and water before continuing sample collection. All disposable PPE such as Tyvek suits, rubber booties, surgeons gloves, respirator cartridges, etc., will be placed in a 55-gallon open top metal drum supplied by TransTechnology who will handle disposal.

7.1 Respirator Decontamination

The steps to be followed for cleaning and disinfecting respirators in the field are as follows:

1. The mask may be washed/rinsed with soap (Liquinox) and water.
2. At a minimum, the mask should be wiped with disinfectant wipes (benzoalkaloid or isopropyl alcohol) and allowed to air dry in a clean area.
3. Visually inspect the entire unit for any obvious damages, defects, or deteriorated rubber.
4. Make sure that the face piece harness is not damaged. The serrated portion of the harness can fragment which will prevent proper face seal adjustment.
5. Inspect lens for damage and proper seal in face piece.
6. Exhalation Valve - Pull off plastic cover and check valve for debris or for tears in the neoprene valve (which could cause leakage).

7. Inhalation Valves (two) - Screw off cartridges/canisters and visually inspect neoprene valves for tears. Make sure that the inhalation valves and cartridge receptacle gaskets are in place.

8. Make sure a protective cover lens is attached to the lens.

9. Make sure the speaking diaphragm retainer ring is hand tight.

10. Make sure that you have the correct cartridge.

11. Don and perform negative pressure test.

8.0 EMERGENCY RESPONSE/CONTINGENCY

Two-way radios will be used to request emergency assistance from TransTechnology Corporation. Communications between the sampling team and TransTechnology Corporation will be established before site work begins. A first aid kit will be available onsite when workers are present. CPR shields and protective gloves will be included in the first aid kit. A portable eyewash will also be accessible. At least two individuals onsite will have a current certification in CPR and/or first aid. In case of skin contact with liquid CNS, remove contaminated clothing, wash with soap or Liquinox and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). If burns occur, cover affected area with sterile, dry, loose-fitting dressing and get medical attention immediately.

8.1 Equipment Decontamination Procedures

For specific equipment decontamination, refer to the sample collection plan, Section 2.2.

8.2 Emergency Contacts

Fire:	911
Police:	911
Ambulance:	911
Hospital:	412/537-1000 Latrobe Area Hospital W. 2nd Street, Latrobe, PA 15650

Directions to Hospital:

Exit plant and turn south toward Tunnelton. Go across the river and turn to nearest right on Pump Station Road. Stay on this road until it meets Rt. 981. Turn left (south) on Rt. 981 to Latrobe (see Figure 1). Stay on Rt. 981 until Ligonier St. Turn right on Ligonier St. then left on W. 2nd Ave. The hospital is two blocks down on the left. Watch for blue and white hospital signs and consult the maps in Figure 2. Driving distance is 15 miles (25 minutes).

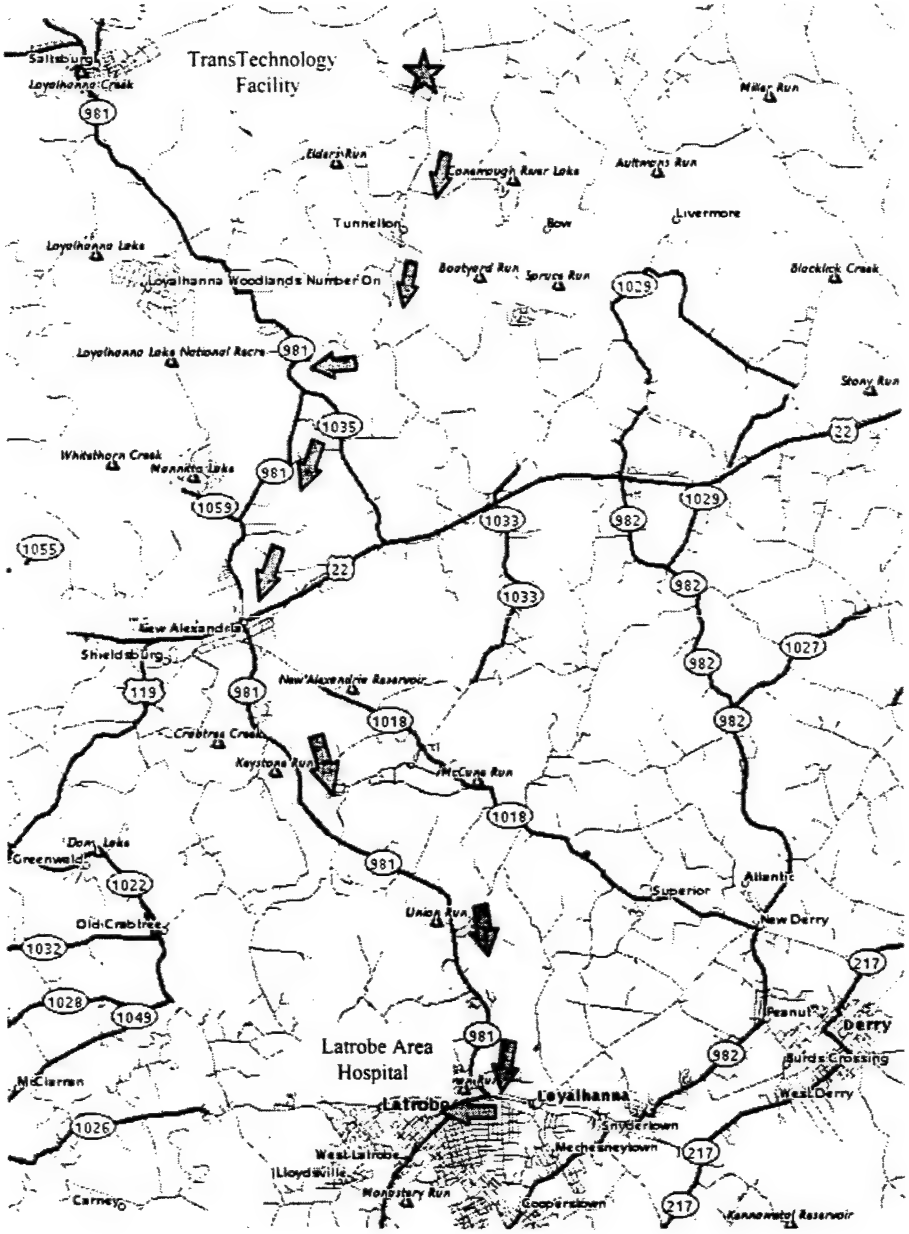

FIGURE 1

Map to Latrobe, PA

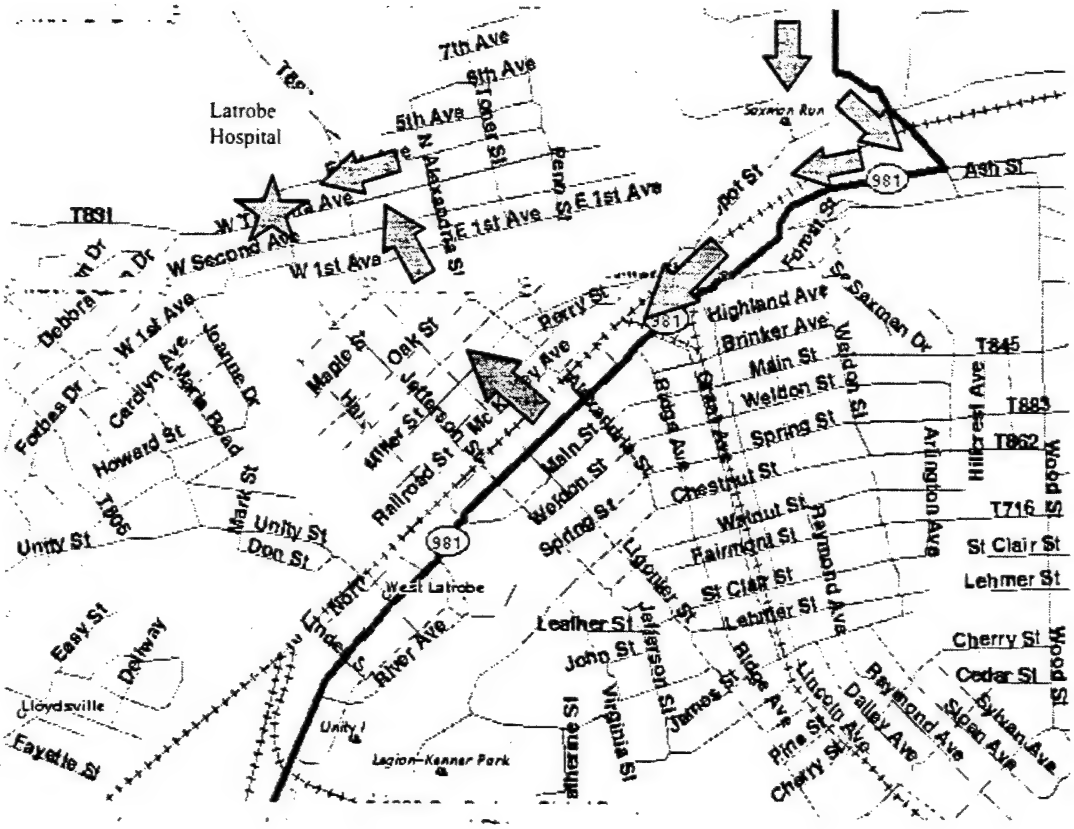

FIGURE 2

Map to Latrobe Area Hospital

Attachment 1

MATERIAL SAFETY DATA SHEETS FOR:

- **CN**
- **CS**
- **CHLOROPICRIN**
- **CHLOROFORM**

Attachment 2

OPERATING INSTRUCTIONS AND SAFETY NOTICE FOR LITTLE BEAVER HYDRAULIC EARTH DRILLS

Attachment 1

MATERIAL SAFETY DATA SHEETS FOR:

- **CN**
- **CS**
- **CHLOROPICRIN**
- **CHLOROFORM**

OHS00780

SECTION 1 CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

MDL INFORMATION SYSTEMS, INC.
14600 CATALINA STREET
SAN LEANDRO, CA 94577
1-800-635-0064 OR
1-510-895-1313

FOR EMERGENCY SOURCE INFORMATION
CONTACT: 1-615-366-2000 USA

CAS NUMBER: 532-27-4
RTECS NUMBER: AM6300000

SUBSTANCE: ALPHA-CHLOROACETOPHENONE

TRADE NAMES/SYNONYMS:
ETHANONE, 2-CHLORO-1-PHENYL-; 2-CHLORO-1-PHENYLETHANONE; ACETOPHENONE, 2-CHLORO-; CHLOROACETOPHENONE; OMEGA-CHLOROACETOPHENONE; 2-CHLOROACETOPHENONE; CHLOROMETHYL PHENYL KETONE; PHENACYL CHLORIDE; PHENYL CHLOROMETHYL KETONE; CHEMICAL MACE; CN; CAF; MACE (LACRIMATOR); MACE; "TEAR GAS"; C8H7CL0; UN 1697; STCC 4925220; OHS00780

CHEMICAL FAMILY:
Ketone

ogen compound, aromatic

CREATION DATE: 06/07/89 REVISION DATE: 06/25/96

SECTION 2 COMPOSITION, INFORMATION ON INGREDIENTS

COMPONENT : ALPHA-CHLOROACETOPHENONE
CAS NUMBER: 532-27-4
PERCENTAGE: 100.0

OTHER CONTAMINANTS: NONE

SECTION 3 HAZARDS IDENTIFICATION

NFPA RATINGS (SCALE 0-4): HEALTH=2 FIRE=1 REACTIVITY=0

EMERGENCY OVERVIEW:
Colorless, white, or gray solid with a sharp irritating odor.
May be fatal if swallowed. Causes respiratory tract burns. Causes skin and eye irritation, possibly severe. May cause allergic skin reaction and lacrimation (irritation and tears).

Poison. Do not breathe dust. Do not get in eyes, on skin, or on clothing. Avoid repeated or prolonged contact. Keep container tightly closed. Wash thoroughly after handling. Use only with adequate ventilation. Handle with caution.

POTENTIAL HEALTH EFFECTS:
INHALATION:
SHORT TERM EFFECTS: May cause burns. Additional effects may include nausea, vomiting, difficulty breathing, high blood pressure, headache, loss of reflexes, tingling sensation, pin-point pupils, lung damage and coma.
LONG TERM EFFECTS: Same effects as short term exposure.
SKIN CONTACT:
SHORT TERM EFFECTS: May cause irritation, possibly severe. May cause allergic reactions.
LONG TERM EFFECTS: Same effects as short term exposure.
EYE CONTACT:
SHORT TERM EFFECTS: May cause irritation, possibly severe. Additional effects may include hair loss, tearing, intolerance of the eyes to light and blindness.
LONG TERM EFFECTS: Same effects as short term exposure.
INGESTION:
SHORT TERM EFFECTS: May be fatal if swallowed.
LONG TERM EFFECTS: No information is available.

CARCINOGEN STATUS:
[redacted]A: N
[redacted]: N
IARC: N

SECTION 4 FIRST AID MEASURES

INHALATION:
FIRST AID- Remove from exposure area to fresh air immediately. Perform artificial respiration if necessary. Maintain airway, blood pressure and respiration. Keep warm and at rest. Treat symptomatically and supportively. Get medical attention immediately. Qualified medical personnel should consider administering oxygen.

SKIN CONTACT:
FIRST AID- Remove contaminated clothing and shoes immediately. Wash with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). If burns occur, proceed with the following: Cover affected area securely with sterile, dry, loose-fitting dressing. Treat symptomatically and supportively. Get medical attention immediately.

EYE CONTACT:
[redacted]

FIRST AID- Wash eyes immediately with large amounts of water, occasionally lifting upper and lower lids, until no evidence of chemical remains (at least 15-20 minutes). Continue irrigating with normal saline until the pH has returned to normal (30-60 minutes). Cover with sterile bandages. Get medical attention immediately.

INGESTION:
FIRST AID- If vomiting does not completely empty the stomach, proceed with the following: Induce emesis with syrup of ipecac and water. When vomiting occurs, keep head lower than hips to help prevent aspiration. Do not give anything by mouth or induce vomiting if person is unconscious or otherwise unable to swallow. Treat symptomatically and supportively. Get medical attention immediately. Qualified medical personnel should consider performing gastric lavage (Dreisbach & Robertson; Handbook of Poisoning; 12th Ed.).

NOTE TO PHYSICIAN
ANTIDOTE:
No specific antidote. Treat symptomatically and supportively.

SECTION 5 FIRE FIGHTING MEASURES

FIRE AND EXPLOSION HAZARD:
Slight fire hazard when exposed to heat or flame.

EXTINGUISHING MEDIA:
dry chemical, carbon dioxide, water spray or regular foam (1993 Emergency Response Guidebook, RSPA P 5800.6).

For larger fires, use water spray, fog or regular foam (1993 Emergency Response Guidebook, RSPA P 5800.6).

FIREFIGHTING:
Move container from fire area if you can do it without risk (1993 Emergency Response Guidebook, RSPA P 5800.6, Guide Page 53).

Use water in flooding amounts as fog. Use alcohol foam, carbon dioxide or dry chemical. Cool containers with flooding amounts of water. Use water spray to absorb vapors. Avoid breathing irritating vapors, keep upwind.

FLASH POINT: 244 F (118 C) (CC)
LOWER FLAMMABLE LIMIT: no data available
UPPER FLAMMABLE LIMIT: no data available
AUTOIGNITION: no data available
FLAMMABILITY CLASS(OSHA): IIIB

HAZARDOUS COMBUSTION PRODUCTS:
Thermal decomposition products may include toxic and corrosive fumes of

chlorides and toxic oxides of carbon.

SECTION 6 ACCIDENTAL RELEASE MEASURES

OCCUPATIONAL SPILL:
Do not touch spilled material. Stop leak if you can do it without risk. For small spills, take up with sand or other absorbent material and place into containers for later disposal. For small dry spills, with a clean shovel place material into clean, dry container and cover. Move containers from spill area. For larger spills, dike far ahead of spill for later disposal. Keep unnecessary people away. Isolate hazard area and deny entry.

SECTION 7 HANDLING AND STORAGE

Observe all federal, state and local regulations when storing this substance.

Store away from incompatible substances.

Store in a tightly closed container.

SECTION 8 EXPOSURE CONTROLS, PERSONAL PROTECTION

EXPOSURE LIMITS:
ALPHA-CHLOROACETOPHENONE:
0.05 ppm (0.3 mg/m3) OSHA TWA
0.05 ppm (0.3 mg/m3) ACGIH TWA
ACGIH A4-Not Classifiable as a Human Carcinogen (Proposed Addition 1995-96)
0.05 ppm (0.3 mg/m3) NIOSH recommended 10 hour TWA

Measurement method: Tenax(R) GC tube (2); thermal desorption apparatus; gas chromatography with flame ionization detection; (NIOSH II(5) # 291, P&CAM).

100 pounds CERCLA Section 103 Reportable Quantity
Subject to SARA Section 313 Annual Toxic Chemical Release Reporting

VENTILATION:
Provide local exhaust or process enclosure ventilation to meet published exposure limits.

EYE PROTECTION:
Employee must wear splash-proof or dust-resistant safety goggles and a faceshield to prevent contact with this substance.

Emergency wash facilities:
Where there is any possibility that an employee's eyes and/or skin may be

exposed to this substance, the employer should provide an eye wash fountain and quick drench shower within the immediate work area for emergency use.

THING:
Employee must wear appropriate protective (impervious) clothing and equipment to prevent any possibility of skin contact with this substance.

GLOVES:
Employee must wear appropriate protective gloves to prevent contact with this substance.

RESPIRATOR:
The following respirators and maximum use concentrations are recommendations by the U.S. Department of Health and Human Services, NIOSH Pocket Guide to Chemical Hazards; NIOSH criteria documents or by the U.S. Department of Labor, 29 CFR 1910 Subpart Z.
The specific respirator selected must be based on contamination levels found in the work place, must not exceed the working limits of the respirator and be jointly approved by the National Institute for Occupational Safety and Health and the Mine Safety and Health Administration (NIOSH-MSHA).

ALPHA-CHLOROACETOPHENONE:

3 mg/m3- Any chemical cartridge respirator with organic vapor cartridge(s) in combination with a dust and mist filter.
Any supplied-air respirator.

mg/m3- Any supplied-air respirator operated in a continuous-flow mode.
Any powered, air-purifying respirator with organic vapor cartridge(s) in combination with a dust and mist filter.

15 mg/m3- Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) in combination with a high-efficiency filter.
Any air-purifying, full facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against this compound and having a high-efficiency particulate filter.
Any self-contained breathing apparatus with a full facepiece.
Any supplied-air respirator with a full facepiece.

Escape- Any air-purifying, full facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against this compound and having a high-efficiency particulate filter.
Any appropriate escape-type, self-contained breathing apparatus.

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:

Any self-contained breathing apparatus that has a full facepiece and is

operated in a pressure-demand or other positive-pressure mode.

Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

DESCRIPTION: Colorless, white, or gray solid with a sharp irritating odor.
MOLECULAR WEIGHT: 154.60
MOLECULAR FORMULA: C6-H5-C-O-C-H2-CL
BOILING POINT: 477 F (247 C)
MELTING POINT: 135 F (57 C)
VAPOR PRESSURE: 0.0012 mmHg @ 20 C
VAPOR DENSITY: 5.32
SPECIFIC GRAVITY: 1.324 @ 15 C
WATER SOLUBILITY: insoluble
PH: not applicable
ODOR THRESHOLD: 0.1 mg/m3
EVAPORATION RATE: (butyl acetate=1.0) <1.0
SOLVENT SOLUBILITY: Soluble in acetone, benzene, carbon disulfide, alcohol, and ether.

SECTION 10 STABILITY AND REACTIVITY

REACTIVITY:
Reacts on contact with water to produce toxic and corrosive vapors.

CONDITIONS TO AVOID:
May burn but does not ignite readily. Prevent dispersion of dust in air. Do not allow spilled material to contaminate water sources.

INCOMPATIBILITIES:
ALPHA-CHLOROACETOPHENONE:
OXIDIZERS (STRONG): Fire and explosion hazard.

HAZARDOUS DECOMPOSITION:
Thermal decomposition products may include toxic and corrosive fumes of chlorides and toxic oxides of carbon.

POLYMERIZATION:
Hazardous polymerization has not been reported to occur under normal temperatures and pressures.

SECTION 11 TOXICOLOGICAL INFORMATION

ALPHA-CHLOROACETOPHENONE:
IRRITATION DATA: 12%/6 hours open skin-rat moderate; 5 mg/24 hours skin-rabbit mild; 12%/6 hours open skin-rabbit moderate; 12%/6 hours open skin-guinea pig moderate; 1 mg eye-rabbit mild; 3 mg eye-rabbit severe.
TOXICITY DATA: 159 mg/m3/20 minutes inhalation-human LCLo; 93 mg/m3/3 minutes inhalation-human TCLo; 20 mg/m3 inhalation-human TCLo; 417 mg/m3/15 minutes inhalation-rat LCLo; 600 mg/m3/15 minutes inhalation-mouse LCLo; 465 mg/m3/20 minutes inhalation-rabbit LCLo; 490 mg/m3/30 minutes inhalation-guinea pig LCLo; 50 mg/kg oral-rat LD50; 139 mg/kg oral-mouse LD50; 118 mg/kg oral-rabbit LD50; 158 mg/kg oral-guinea pig LD50; 36 mg/kg intraperitoneal-rat LD50; 60 mg/kg intraperitoneal-mouse LD50; 17 mg/kg intraperitoneal-guinea pig LD50; 41 mg/kg intravenous-rat LD50; 81 mg/kg intravenous-mouse LD50; 30 mg/kg intravenous-rabbit LD50; tumorigenic data (RTECS).
CARCINOGEN STATUS: None.
LOCAL EFFECTS: Corrosive- inhalation, skin, eye; lacrimator.
ACUTE TOXICITY LEVEL: Highly toxic by ingestion.
TARGET EFFECTS: Sensitizer- dermal. Poisoning may also affect the respiratory system.
AT INCREASED RISK FROM EXPOSURE: Persons with pre-existing respiratory, skin, or eye disorders.
ADDITIONAL DATA: May cross react with dichloroacetophenone and o-chlorobenzylidene malononitrile.

HEALTH EFFECTS
INHALATION:
ALPHA-CHLOROACETOPHENONE:
CORROSIVE. 15 mg/m3 Immediately Dangerous to Life or Health.
ACUTE EXPOSURE- Irritation of the mucous membranes occurs readily at 40 mg/m3. Human volunteers exposed to levels of 200-340 mg/m3 could not tolerate exposure for longer than 30 seconds. Symptoms included tingling of the nose, rhinorrhea, coughing, sneezing, burning of the throat and chest, dyspnea and nausea. Other symptoms may include laryngospasm, excessive salivation, bronchorrhea, bronchospasm, a feeling of heat, headache, hypertension, vomiting, agitation, miosis, paresthesia, areflexia, coma, and fatty infiltration of the liver. Severe exposure may cause pulmonary congestion, edema, and death, with the onset of edema delayed, sometimes as long as several days. A small number of deaths have been reported due to pulmonary injury and/or asphyxia after exposure in confined spaces. 0.85 mg/L for 10 minutes is estimated to be the lethal concentration in man.
CHRONIC EXPOSURE- In 2 year studies, mice exposed to 2 or 4 mg/m3 exhibited rapid, shallow breathing during the first 6 months; hyperplasia and squamous metaplasia of the nasal respiratory epithelium were observed in rats and mice.

SKIN CONTACT:
ALPHA-CHLOROACETOPHENONE:

CORROSIVE/SENSITIZER.
ACUTE EXPOSURE- May cause irritation, characterized by purpura, erythema, desquamation, and vesication. Irritant dermatitis may occur, particularly in blonds or persons with light pigmentation. Changes in pigmentation, which may be persistent and disfiguring in black skin, have been reported. Allergic contact dermatitis often accompanied by marked edema may also occur. A delayed necrotic eschar has been reported in rabbits after a massive vapor exposure.
CHRONIC EXPOSURE- Repeated or prolonged contact may lead to sensitization dermatitis. When applied to the skin of mice previously given dermal applications of 0.3 mL of 0.15% 9,10-dimethyl-1,2-benzanthracene, there was an increased incidence of epidermal papillomas.

EYE CONTACT:
ALPHA-CHLOROACETOPHENONE:
CORROSIVE/LACRIMATOR.
ACUTE EXPOSURE- Vapor may cause irritation, profuse lacrimation, intense stinging and burning and involuntary closure of the eyes, spasm of the lids, photophobia, marked conjunctivitis, corneal haziness, blurred vision and temporary blindness. These effects are usually transient with complete recovery within a few days. However, if eyes are excessively contaminated by the vapor or solid, severe and permanent corneal injury including burns and scarring may occur. Permanent opacification, and ulceration with vascularization and perforation has been produced in animals. Additional effects noted in rabbits after application of 10-20% solution included chemosis, iritis, depilation, and lid disfigurement.
CHRONIC EXPOSURE- Repeated or prolonged exposure may result in conjunctivitis.

INGESTION:
ALPHA-CHLOROACETOPHENONE:
HIGHLY TOXIC.
ACUTE EXPOSURE- The lethal dose reported in rats was 50 mg/kg. The symptoms were not reported.
CHRONIC EXPOSURE- No data available.

SECTION 12 ECOLOGICAL INFORMATION

ENVIRONMENTAL IMPACT RATING (0-4): no data available

ACUTE AQUATIC TOXICITY: no data available

DEGRADABILITY: no data available

LOG BIOCONCENTRATION FACTOR (BCF): no data available

LOG OCTANOL/WATER PARTITION COEFFICIENT: no data available

SECTION 13 DISPOSAL CONSIDERATIONS

Observe all federal, state and local regulations when disposing of this substance.

SECTION 14 TRANSPORT INFORMATION

U.S. DEPARTMENT OF TRANSPORTATION SHIPPING NAME-ID NUMBER, 49 CFR 172.101:
Chloracetophenone, solid-UN 1697

U.S. DEPARTMENT OF TRANSPORTATION HAZARD CLASS OR DIVISION, 49 CFR 172.101:
6.1 - Poisonous materials

U.S. DEPARTMENT OF TRANSPORTATION PACKING GROUP, 49 CFR 172.101:
PG II

U.S. DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS, 49 CFR 172.101 AND SUBPART E:
Poison

U.S. DEPARTMENT OF TRANSPORTATION PACKAGING AUTHORIZATIONS:
EXCEPTIONS: None
NON-BULK PACKAGING: 49 CFR 173.212
BULK PACKAGING: None

U.S. DEPARTMENT OF TRANSPORTATION QUANTITY LIMITATIONS 49 CFR 172.101:
PASSENGER AIRCRAFT OR RAILCAR: Forbidden
CARGO AIRCRAFT ONLY: 100 kg

SECTION 15 REGULATORY INFORMATION

TSCA INVENTORY STATUS: Y

CERCLA SECTION 103 (40CFR302.4):	Y	
ALPHA-CHLOROACETOPHENONE		100 pounds RQ
SARA SECTION 302 (40CFR355.30):	N	
SARA SECTION 304 (40CFR355.40):	N	
SARA SECTION 313 (40CFR372.65):	Y	
ALPHA-CHLOROACETOPHENONE		
OSHA PROCESS SAFETY (29CFR1910.119):	N	
CALIFORNIA PROPOSITION 65:	N	

SARA HAZARD CATEGORIES, SARA SECTIONS 311/312 (40 CFR 370.21)

ACUTE HAZARD:	Y
CHRONIC HAZARD:	Y
FIRE HAZARD:	N

REACTIVITY HAZARD: Y
SUDDEN RELEASE HAZARD: N

SECTION 16 OTHER INFORMATION

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OHS16910

SECTION 1 CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

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CONTACT: 1-615-366-2000 USA

CAS NUMBER: 2698-41-1
RTECS NUMBER: OO3675000

SUBSTANCE: O-CHLOROBENZYLIDENE MALONONITRILE

TRADE NAMES/SYNONYMS:
PROPANEDINITRILE, ((2-CHLOROPHENYL)METHYLENE)-;
((2-CHLOROPHENYL)METHYLENE)PROPANEDINITRILE;
MALONONITRILE, (O-CHLOROBENZYLIDENE)-; (O-CHLOROBENZYLIDENE)MALONONITRILE;
(O-CHLOROBENZAL)MALONONITRILE; 2-CHLOROBENZALMALONONITRILE;
O-CHLOROBENZYLIDENEMALONONITRILE; 2-CHLOROBENZYLIDENEMALONONITRILE;
2-CHLOROBENZYLIDENE MALONONITRILE; BETA,BETA-DICYANO-O-CHLOROSTYRENE;
BETA,BETA-DICYANO-ORTHO-CHLOROSTYRENE; CS; OCBM;
O-CHLOROBENZYLIDENEMALONIC NITRILE; C10H5CLN2; OHS16910

CHEMICAL FAMILY:
Styrene

Cyanide

Halogen compound, aromatic

CREATION DATE: 02/06/86 REVISION DATE: 01/05/96

SECTION 2 COMPOSITION, INFORMATION ON INGREDIENTS

COMPONENT : O-CHLOROBENZYLIDENE MALONONITRILE
CAS NUMBER: 2698-41-1
PERCENTAGE: 100.0

OTHER CONTAMINANTS: NONE

SECTION 3 HAZARDS IDENTIFICATION

NFPA RATINGS (SCALE 0-4): HEALTH=2 FIRE=1 REACTIVITY=0

EMERGENCY OVERVIEW:
White crystals or solid with a pepper-like odor.
Harmful if swallowed. Causes respiratory tract, skin, and eye irritation. May cause allergic skin reaction and lacrimation (irritation and tears). Avoid breathing dust. Avoid contact with eyes, skin and clothing. Avoid repeated or prolonged contact. Keep container tightly closed. Wash thoroughly after handling. Use only with adequate ventilation. Handle with caution.

POTENTIAL HEALTH EFFECTS:
INHALATION:
SHORT TERM EFFECTS: May cause irritation. Additional effects may include nausea, vomiting, difficulty breathing, headache, dizziness, lung congestion, kidney damage and heart failure.
LONG TERM EFFECTS: No information available on significant adverse effects.
SKIN CONTACT:
SHORT TERM EFFECTS: May cause irritation. May cause allergic reactions. Additional effects may include blisters and burns.
LONG TERM EFFECTS: Same effects as short term exposure.
EYE CONTACT:
SHORT TERM EFFECTS: May cause irritation. Additional effects may include redness of the skin, tearing, intolerance of the eyes to light and blindness.
LONG TERM EFFECTS: Same effects as short term exposure.
INGESTION:
SHORT TERM EFFECTS: May be harmful if swallowed. May cause diarrhea, twitching and convulsions.
LONG TERM EFFECTS: No information is available.

CARCINOGEN STATUS:
OSHA: N
NTP: N
IARC: N

SECTION 4 FIRST AID MEASURES

INHALATION:
FIRST AID- Remove from exposure area to fresh air immediately. Perform artificial respiration if necessary. Keep person warm and at rest. Treat symptomatically and supportively. Get medical attention immediately.

SKIN CONTACT:
FIRST AID- Remove contaminated clothing and shoes immediately. Wash with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). Get medical attention immediately.

EYE CONTACT:
FIRST AID- Wash eyes immediately with large amounts of water or normal saline, occasionally lifting upper and lower lids, until no evidence of chemical remains (at least 15-20 minutes). Get medical attention immediately.

INGESTION:
FIRST AID- If vomiting does not completely empty the stomach, proceed with the following: Induce emesis with syrup of ipecac and water. When vomiting occurs, keep head lower than hips to help prevent aspiration. Do not give anything by mouth or induce vomiting if person is unconscious or otherwise unable to swallow. Treat symptomatically and supportively. Get medical attention immediately. Qualified medical personnel should consider performing gastric lavage (Dreisbach & Robertson; Handbook of Poisoning; 12th Ed.).

NOTE TO PHYSICIAN
ANTIDOTE:
No specific antidote. Treat symptomatically and supportively.

SECTION 5 FIRE FIGHTING MEASURES

FIRE AND EXPLOSION HAZARD:
Slight fire hazard when exposed to heat or flame.

EXTINGUISHING MEDIA:
dry chemical, carbon dioxide, water spray or regular foam (1993 Emergency Response Guidebook, RSPA P 5800.6).

For larger fires, use water spray, fog or regular foam (1993 Emergency Response Guidebook, RSPA P 5800.6).

FIREFIGHTING:
Move container from fire area if you can do it without risk (1993 Emergency Response Guidebook, RSPA P 5800.6, Guide Page 53).

Extinguish using agent suitable for type of surrounding fire. Avoid breathing vapors and dusts. Keep upwind.

FLASH POINT: no data available
LOWER FLAMMABLE LIMIT: 0.025 g/L
UPPER FLAMMABLE LIMIT: no data available
AUTOIGNITION: no data available

HAZARDOUS COMBUSTION PRODUCTS:
Thermal decomposition may release corrosive fumes of hydrogen chloride or toxic chlorine gas, hydrogen cyanide, and oxides of carbon and nitrogen.

SECTION 6 ACCIDENTAL RELEASE MEASURES

OCCUPATIONAL SPILL:
Do not touch spilled material. Stop leak if you can do it without risk. For small spills, take up with sand or other absorbent material and place into containers for later disposal. For small dry spills, with a clean shovel place material into clean, dry container and cover. Move containers from spill area. For larger spills, dike far ahead of spill for later disposal. Keep unnecessary people away. Isolate hazard area and deny entry.

SECTION 7 HANDLING AND STORAGE

Observe all federal, state and local regulations when storing this substance.

Store away from incompatible substances.

SECTION 8 EXPOSURE CONTROLS, PERSONAL PROTECTION

EXPOSURE LIMITS:
O-CHLOROBENZYLIDENE MALONONITRILE:
0.05 PPM (0.4 mg/m3) OSHA TWA
0.05 ppm (0.4 mg/m3) OSHA ceiling (skin) (vacated by 58 FR 35338, June 30, 1993)
0.05 ppm (0.4 mg/m3) ACGIH ceiling (skin)
ACGIH A4-Not Classifiable as a Human Carcinogen (Proposed Addition 1995-96)
0.05 ppm (0.4 mg/m3) NIOSH recommended ceiling (skin)

Measurement method: Particulate filter/Tenax(R) GC tube; reagent; high-pressure liquid chromatography with ultraviolet detection; (NIOSH II(5) # 304, P&CAM).

VENTILATION:
Provide local exhaust ventilation system to meet published exposure limits.

EYE PROTECTION:
Employee must wear splash-proof or dust-resistant safety goggles to prevent contact with this substance.

Emergency wash facilities:
Where there is any possibility that an employee's eyes and/or skin may be exposed to this substance, the employer should provide an eye wash fountain and quick drench shower within the immediate work area for emergency use.

CLOTHING:
Employee must wear appropriate protective (impervious) clothing and equipment to prevent repeated or prolonged skin contact with this substance.

GLOVES:
Employee must wear appropriate protective gloves to prevent contact with this substance.

RESPIRATOR:
The following respirators and maximum use concentrations are recommendations by the U.S. Department of Health and Human Services, NIOSH Pocket Guide to Chemical Hazards; NIOSH criteria documents or by the U.S. Department of Labor, 29 CFR 1910 Subpart Z.
The specific respirator selected must be based on contamination levels found in the work place, must not exceed the working limits of the respirator and be jointly approved by the National Institute for Occupational Safety and Health and the Mine Safety and Health Administration (NIOSH-MSHA).

O-CHLOROBENZYLIDENE MALONONITRILE:
2 mg/m3 - Any supplied-air respirator operated in a continuous flow-mode.
Any air-purifying, full facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against this compound and having a high-efficiency particulate filter.
Any self-contained breathing apparatus with a full facepiece.
Any supplied-air respirator with a full facepiece.

Escape- Any air-purifying, full facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against this compound and having a high-efficiency particulate filter.
Any appropriate escape-type, self-contained breathing apparatus.

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:

Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode.

Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

DESCRIPTION: White crystals or solid with a pepper-like odor.
MOLECULAR WEIGHT: 188.61
MOLECULAR FORMULA: C10-H5-CL-N2
BOILING POINT: 590-599 F (310-315 C)
MELTING POINT: 203-205 F (95-96 C)
VAPOR PRESSURE: negligible
VAPOR DENSITY: 6.52

SPECIFIC GRAVITY: >1
WATER SOLUBILITY: 0.008% @ 25 C
VOLATILITY: <1%
[redacted] not applicable
ODOR THRESHOLD: no data available
EVAPORATION RATE: not applicable
SOLVENT SOLUBILITY: Soluble in acetone, dioxane, methylene chloride, ethyl acetate and benzene; less soluble in ethanol.

SECTION 10 STABILITY AND REACTIVITY

REACTIVITY:
Stable under normal temperatures and pressures.

CONDITIONS TO AVOID:
May burn but does not ignite readily. Prevent dispersion of dust in air. Do not allow spilled material to contaminate water sources.

INCOMPATIBILITIES:
O-CHLOROBENZYLIDENE MALONONITRILE:
OXIDIZERS (STRONG): Fire and explosion hazard.

HAZARDOUS DECOMPOSITION:
Thermal decomposition may release corrosive fumes of hydrogen chloride or toxic chlorine gas, hydrogen cyanide, and oxides of carbon and nitrogen.

POLYMERIZATION:
Hazardous polymerization has not been reported to occur under normal temperatures and pressures.

SECTION 11 TOXICOLOGICAL INFORMATION

O-CHLOROBENZYLIDENE MALONONITRILE:
IRRITATION DATA: 10 mg/1 hour skin-human mild; 12%/6 hours open skin-rabbit mild; 12%/6 hours open skin-rat mild; 12%/6 hours open skin-guinea pig mild; 5 mg/m3/20 seconds eye-man severe; 624 ng eye-man; 5 mg eye-rabbit; 1 mg eye-rabbit mild; 1150 ng eye-rabbit; 429 ng eye-guinea pig.
TOXICITY DATA: 1500 ug/m3/90 minutes inhalation-human TCLo; 1806 mg/m3/45 minutes inhalation-rat LCLo; 2753 mg/m3/20 minutes inhalation-mouse LCLo; 1802 mg/m3/10 minutes inhalation-rabbit LCLo; 2326 mg/m3/10 minutes inhalation-guinea pig LCLo; 88480 mg/m3/1 minute inhalation-rat LC50 (MEIEDD); 178 mg/kg oral-rat LD50; 282 mg/kg oral-mouse LD50; 143 mg/kg oral-rabbit LD50; 212 mg/kg oral-guinea pig LD50; 28 mg/kg intravenous-rat LD50; 47700 ug/kg intravenous-mouse LD50; 8 mg/kg intravenous-rabbit LDLo; 48 mg/kg intraperitoneal-rat LD50; 32320 ug/kg intraperitoneal-mouse LD50; 73 mg/kg intraperitoneal-guinea pig LD50; mutagenic data (RTECS); reproductive effects data (RTECS).

CARCINOGEN STATUS: None.
LOCAL EFFECTS: Irritant- inhalation, skin, eye; lacrimator.
ACUTE TOXICITY LEVEL: Toxic by ingestion; moderately toxic by inhalation.
TARGET EFFECTS: Sensitizer- skin. Poisoning may also affect the respiratory system, liver, and kidneys.
AT INCREASED RISK FROM EXPOSURE: Persons with chronic respiratory, skin, or eye disease. Light pigmented people may acquire irritation dermatitis more readily.

HEALTH EFFECTS
INHALATION:
O-CHLOROBENZYLIDENE MALONONITRILE:
IRRITANT. 2 mg/m3 Immediately Dangerous to Life or Health.
ACUTE EXPOSURE- 1-6.7 mg/m3 has produced respiratory tract irritation and a burning sensation, cough, rhinorrhea, salivation, sneezing, epistaxis, headache, lethargy, dyspnea, constricted feeling in the chest, progressive respiratory depression, and loss of respiratory control. Additional symptoms may include nausea, vomiting, and dizziness. Concentrations >10 mg/m3 were intolerable for more than 30 seconds. Pulmonary edema complicated by pneumonia, heart failure, and hepatocellular damage were observed in a 43 year old male exposed to this compound. Exposure to 150-480 mg/m3 produced pulmonary edema, liver necrosis, acute renal tubular necrosis, and some deaths in animals. At 20,000 mg/minute/m3 mice metabolized o-chlorobenzylidene malononitrile to cyanide, but its extreme irritancy makes the reaction unlikely to occur in humans.
CHRONIC EXPOSURE- Repeated or prolonged exposure may cause loss of the sense of taste. 7 men exposed to 1-13 mg/m3 10 times over a 15 day period showed no clinical abnormalities except one case of rising thymol turbidity. Animals exposed to 300 ug/L for 1 hour a day, 5 days a week, for up to 120 days showed a significant increase in mortality. Reproductive effects have been reported in animals.

SKIN CONTACT:
O-CHLOROBENZYLIDENE MALONONITRILE:
IRRITANT/SENSITIZER.
ACUTE EXPOSURE- May cause irritation with mild pain and local erythema. When moist or occluded, irritation may be severe with stinging, vesiculation, burns, and possibly ulceration. Sensitization dermatitis may occur in previously exposed individuals. In guinea pigs, cross-reactions with 1-chloroacetphenone have been reported.
CHRONIC EXPOSURE- 25 of 28 workers had a history of dermatitis on the neck and arms. Repeated or prolonged contact may lead to sensitization dermatitis.

EYE CONTACT:
O-CHLOROBENZYLIDENE MALONONITRILE:
IRRITANT/LACRIMATOR.
ACUTE EXPOSURE- May cause burning pain, lacrimation, involuntary closing of the eyes due to blepharospasm, blurred vision, photophobia,

and temporary blindness. Severe conjunctival injection and erythema of the eyelids may occur and last up to 1 hour after exposure.
Humans exposed to concentrations >5 mg/m3 could not keep their eyes open for even a few seconds due to the intense irritation, but visual acuity returned to normal within a few minutes after exposure was terminated. 0.05-0.1 mL of a 10-50% solution applied directly to rabbit eyes caused immediate and severe irritation persisting for 30-60 minutes and erythema of the iris lasting up to 48 hours, but no permanent damage. Small particles caused greater irritation, but large particles caused increased recovery time.

CHRONIC EXPOSURE- Repeated or prolonged exposure to irritants may cause conjunctivitis.

INGESTION:
O-CHLOROBENZYLIDENE MALONONITRILE:
TOXIC.

ACUTE EXPOSURE- Administration to animals produced pilo-erection, increased salivation, diarrhea, tremors, rapid shallow breathing, reduced locomotion, hemorrhagic erosion of the gastric mucosa, convulsions, collapse, and death.

CHRONIC EXPOSURE- No data available.

SECTION 12 ECOLOGICAL INFORMATION

ENVIRONMENTAL IMPACT RATING (0-4): no data available

ACUTE AQUATIC TOXICITY: no data available

DEGRADABILITY: no data available

LOG BIOCONCENTRATION FACTOR (BCF): no data available

LOG OCTANOL/WATER PARTITION COEFFICIENT: no data available

SECTION 13 DISPOSAL CONSIDERATIONS

Observe all federal, state and local regulations when disposing of this substance.

SECTION 14 TRANSPORT INFORMATION

No classification currently assigned

SECTION 15 REGULATORY INFORMATION

TSCA INVENTORY STATUS: Y

CLA SECTION 103 (40CFR302.4):	N
A SECTION 302 (40CFR355.30):	N
SARA SECTION 304 (40CFR355.40):	N
SARA SECTION 313 (40CFR372.65):	N
OSHA PROCESS SAFETY (29CFR1910.119):	N
CALIFORNIA PROPOSITION 65:	N

SARA HAZARD CATEGORIES, SARA SECTIONS 311/312 (40 CFR 370.21)

ACUTE HAZARD:	Y
CHRONIC HAZARD:	Y
FIRE HAZARD:	N
REACTIVITY HAZARD:	N
SUDDEN RELEASE HAZARD:	N

SECTION 16 OTHER INFORMATION

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OHS04830

SECTION 1 CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

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CAS NUMBER: 76-06-2
RTECS NUMBER: PB6300000

SUBSTANCE: CHLOROPICRIN

TRADE NAMES/SYNONYMS:
NITROCHLOROMETHANE; TRICHLORONITROMETHANE; PICRIDE; CHLOR-O-PIC; PICFUME; TRI-CLOR; CHLOROPICRIN, LIQUID; AQUINITE; DOLOCHLOR; G 25; LARVACIDE; MICROLYSIN; PROFUME A; S 1; NITROCHLOROFORM; PIC-CLOR; PS; UN 1580; STCC 4921414; OHS04830

CHEMICAL FAMILY:
Nitro

Halogen compound, aliphatic

CREATION DATE: 10/31/85 REVISION DATE: 01/24/96

SECTION 2 COMPOSITION, INFORMATION ON INGREDIENTS

COMPONENT : CHLOROPICRIN
CAS NUMBER: 76-06-2
PERCENTAGE: 100

OTHER CONTAMINANTS: NONE

SECTION 3 HAZARDS IDENTIFICATION

NFPA RATINGS (SCALE 0-4): HEALTH=4 FIRE=0 REACTIVITY=3

EMERGENCY OVERVIEW:
Oily, colorless liquid, extremely irritating odor.
May be fatal if inhaled. Harmful if swallowed. Causes severe burns to mucous membranes. Causes respiratory tract, skin, and eye irritation, possibly severe. May cause lacrimation (irritation and tears). May affect blood cells.

May explode from heat, shock or friction.
Poison. Do not breathe vapor or mist. Do not get in eyes, on skin, or on clothing. Keep away from heat, sparks, and flame. Avoid contamination by any source. Keep container tightly closed. Wash thoroughly after handling. Use only with adequate ventilation. Do not subject to heat or shock.

POTENTIAL HEALTH EFFECTS:
INHALATION:
SHORT TERM EFFECTS: May be fatal if inhaled. May cause irritation, possibly severe. Additional effects may include nausea, vomiting, difficulty breathing, headache, dizziness, bluish skin color and lung congestion.
LONG TERM EFFECTS: In addition to effects from short term exposure, lung damage and coma may occur.
SKIN CONTACT:
SHORT TERM EFFECTS: May cause irritation, possibly severe. Additional effects may include difficulty breathing, headache and bluish skin color.
LONG TERM EFFECTS: Same effects as short term exposure.
EYE CONTACT:
SHORT TERM EFFECTS: May cause irritation, possibly severe. Additional effects may include tearing and eye damage.
LONG TERM EFFECTS: Same effects as short term exposure.
INGESTION:
SHORT TERM EFFECTS: May be harmful if swallowed. May cause burns. Additional effects may include sore throat, vomiting, digestive disorders, difficulty breathing, headache, dizziness and bluish skin color.
LONG TERM EFFECTS: May cause effects as in short term exposure. Additional effects may include lung damage.

CARCINOGEN STATUS:
OSHA: N
NTP: N
IARC: N

SECTION 4 FIRST AID MEASURES

INHALATION:
FIRST AID- Remove from exposure area to fresh air immediately. Perform artificial respiration if necessary. Maintain airway, blood pressure and respiration. Keep warm and at rest. Treat symptomatically and supportively. Get medical attention immediately. Qualified medical personnel should consider administering oxygen.

SKIN CONTACT:
FIRST AID- Remove contaminated clothing and shoes immediately. Wash with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). If burns occur, proceed with the following: Cover affected area securely with sterile, dry, loose-fitting

dressing. Treat symptomatically and supportively. Get medical attention immediately.

CONTACT:
FIRST AID- Wash eyes immediately with large amounts of water, occasionally lifting upper and lower lids, until no evidence of chemical remains (at least 15-20 minutes). Continue irrigating with normal saline until the pH has returned to normal (30-60 minutes). Cover with sterile bandages. Get medical attention immediately.

INGESTION:
FIRST AID- Remove by gastric lavage or emesis using activated charcoal. (Dreisbach, Handbook of Poisoning, 11th Edition) gastric lavage or emesis should not be performed on an unconscious person. Treatment should be administered by qualified medical personnel. Get medical attention immediately.

NOTE TO PHYSICIAN
ANTIDOTE:
The following antidote has been recommended. However, the decision as to whether the severity of poisoning requires administration of any antidote and actual dose required should be made by qualified medical personnel.

METHEMOGLOBINEMIA:
(When methemoglobin concentration is over 25-40% or in presence of symptoms.) Give methylene blue, 1% solution, 0.1 mL/kg intravenously over a 10-minute period. Cyanosis may disappear within minutes or persist longer depending on degree of methemoglobinemia. Intravenous administration of therapeutic doses of methylene blue may cause a rise in blood pressure, nausea, and dizziness. Larger doses (>500 mg) cause vomiting, diarrhea, chest pain, mental confusion, cyanosis, and sweating. Hemolytic anemia has also occurred several days after administration. These effects are temporary, and fatalities have not been reported. If methylene blue is not available, give ascorbic acid, 1 gram slowly intravenously. Without treatment, methemoglobinemia levels of 20-30% revert to normal within 3 days (Dreisbach, Handbook of Poisoning, 12th Ed.). Antidote should be administered by qualified medical personnel.

SECTION 5 FIRE FIGHTING MEASURES

FIRE AND EXPLOSION HAZARD:
Negligible fire hazard when exposed to heat or flame.

EXTINGUISHING MEDIA:
Dry chemical, carbon dioxide, water spray or regular foam (1993 Emergency Response Guidebook, RSPA P 5800.6).

For larger fires, use water spray, fog or regular foam (1993 Emergency Response Guidebook, RSPA P 5800.6).

FIREFIGHTING:
Move container from fire area if you can do it without risk. Apply cooling water to sides of containers that are exposed to flames until well after fire is out. Stay away from ends of tanks. For massive fire in cargo area, use hose holder or monitor nozzles; if this is impossible, withdraw from area and let fire burn (1993 Emergency Response Guidebook, RSPA P 5800.6, Guide Page 56).

Extinguish using agents suitable for type of surrounding fire. Use flooding amounts of water as fog. Avoid breathing poisonous vapors; keep upwind. Consider evacuation of downwind area if material is leaking.

FLASH POINT: nonflammable
LOWER FLAMMABLE LIMIT: no data available
UPPER FLAMMABLE LIMIT: no data available
AUTOIGNITION: no data available

HAZARDOUS COMBUSTION PRODUCTS:
CHLOROPICRIN:
Thermal decomposition produces corrosive fumes of hydrogen chloride and toxic oxides of nitrogen and carbon.

SECTION 6 ACCIDENTAL RELEASE MEASURES

OCCUPATIONAL SPILL:
Do not touch spilled material. Stop leak if you can do it without risk. Use water spray to reduce vapors. For small spills, take up with sand or other absorbent material and place into containers for later disposal. For small dry spills, with clean shovel place material into clean, dry containers and cover. Move containers from spill area. For larger spills, dike far ahead of spill for later disposal. Keep unnecessary people away. Isolate hazard area and deny entry. Ventilate closed spaces before entering.

SECTION 7 HANDLING AND STORAGE

Observe all federal, state and local regulations when storing this substance.

Protect against physical damage. Outside or detached storage is preferred. Inside storage should be in a well-ventilated area. (NFPA 49, Hazardous Chemicals Data, 1975).

Store away from incompatible substances.

Threshold quantity (TQ): 500 pounds
The Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) standard requires that facilities utilizing a process which involves a chemical at or above its specified threshold quantity comply with

the provisions of 29 CFR 1910.119, Process Safety Management of highly hazardous chemicals.

SECTION 8 EXPOSURE CONTROLS, PERSONAL PROTECTION

EXPOSURE LIMITS:
CHLOROPICRIN:
0.1 ppm (0.7 mg/m3) OSHA TWA
0.1 ppm (0.7 mg/m3) ACGIH TWA
ACGIH A4-Not Classifiable as a Human Carcinogen (Proposed Addition 1995-96)
0.1 ppm (0.7 mg/m3) NIOSH recommended 10 hour TWA
0.1 ppm (0.7 mg/m3) DFG MAK TWA;
0.2 ppm (1.4 mg/m3) DFG MAK 5 minute peak, momentary value, 8 times/shift

500 pounds OSHA Process Safety Management Threshold Quantity
Subject to SARA Section 313 Annual Toxic Chemical Release Reporting

VENTILATION:
Provide local exhaust or process enclosure ventilation to meet published exposure limits.

EYE PROTECTION:
Employee must wear splash-proof or dust-resistant safety goggles and a faceshield to prevent contact with this substance.

Emergency wash facilities:
Where there is any possibility that an employee's eyes and/or skin may be exposed to this substance, the employer should provide an eye wash fountain and quick drench shower within the immediate work area for emergency use.

CLOTHING:
Employee must wear appropriate protective (impervious) clothing and equipment to prevent any possibility of skin contact with this substance.

GLOVES:
Employee must wear appropriate protective gloves to prevent contact with this substance.

RESPIRATOR:
The following respirators and maximum use concentrations are recommendations by the U.S. Department of Health and Human Services, NIOSH Pocket Guide to Chemical Hazards; NIOSH criteria documents or by the U.S. Department of Labor, 29 CFR 1910 Subpart Z.
The specific respirator selected must be based on contamination levels found in the work place, must not exceed the working limits of the respirator and be jointly approved by the National Institute for Occupational Safety and Health and the Mine Safety and Health Administration (NIOSH-MSHA).

CHLOROPICRIN:
2 ppm- Any supplied-air respirator operated in a continuous-flow mode.
Any powered, air-purifying respirator with organic vapor cartridge(s).
Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s).
Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted organic vapor canister.
Any self-contained breathing apparatus with a full facepiece.
Any supplied-air respirator with a full facepiece.

Escape- Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted organic vapor canister.
Any appropriate escape-type, self-contained breathing apparatus.

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:

Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode.

Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

DESCRIPTION: Oily, colorless liquid, extremely irritating odor.
MOLECULAR FORMULA: C-CL3-N-O2 MOL WT: 164.37
BOILING POINT: 233 F (112 C)
FREEZING POINT: -83 F (-64 C)
VAPOR PRESSURE: 20 mmHg @ 20 C
VAPOR DENSITY: 5.7
SPECIFIC GRAVITY: 1.7
WATER SOLUBILITY: 0.2% @ 20 C
PH: no data available
ODOR THRESHOLD: 1.1 ppm
EVAPORATION RATE: no data available
SOLVENT SOLUBILITY: Soluble in alcohol, ether, acetone, benzene, acetic acid.

SECTION 10 STABILITY AND REACTIVITY

REACTIVITY:
CHLOROPICRIN:
Bulk containers can be shock detonated.

CONDITIONS TO AVOID:
May burn but does not ignite readily. May explode from friction, heat or contamination.

INCOMPATIBILITIES:
CHLOROPICRIN:
ANILINE: Violent reaction.
BROMO-2-PROPYNE: Explosive, shock- and heat- sensitive.
SODIUM HYDROXIDE: Reacts violently
SODIUM METHOXIDE: Below 50 C, nitro compound will accumulate and cause a violent and dangerous exothermic reaction.
STRONG OXIDIZERS: Possible violent reaction.

HAZARDOUS DECOMPOSITION:
CHLOROPICRIN:
Thermal decomposition produces corrosive fumes of hydrogen chloride and toxic oxides of nitrogen and carbon.

POLYMERIZATION:
Hazardous polymerization has not been reported to occur under normal temperatures and pressures.

SECTION 11 TOXICOLOGICAL INFORMATION

CHLOROPICRIN:
TOXICITY DATA: 2 mg/m3 inhalation-human TCLo; 2000 mg/m3/10 minutes inhalation-human LCLo; 66 mg/m3/4 hours inhalation-mouse LC50; 800 mg/m3/20 minutes inhalation-cat LCLo; 800 mg/m3/20 minutes inhalation-rabbit LC50; 800 mg/m3/20 minutes inhalation-guinea pig LCLo; 14400 ppb/4 hours inhalation-rat LC50; 250 mg/kg oral-rat LD50; 4200 ug/kg intravenous-guinea pig LD50; 25 mg/kg intraperitoneal-mouse LD50; mutagenic data (RTECS); tumorigenic data (RTECS).
CARCINOGEN STATUS: None.
LOCAL EFFECTS: Corrosive- inhalation, skin, and eyes; lacrimator.
ACUTE TOXICITY LEVEL: Highly toxic by inhalation; toxic by ingestion.
TARGET EFFECTS: Methemoglobin former. Poisoning may affect the respiratory and cardiovascular systems.

HEALTH EFFECTS
INHALATION:
CHLOROPICRIN:
CORROSIVE/METHEMOGLOBIN FORMER/HIGHLY TOXIC.
2 ppm Immediately Dangerous to Life or Health.
ACUTE EXPOSURE- May cause irritation, sore throat, coughing, labored breathing, dizziness, nausea, vomiting, cyanosis, faintness, and pulmonary edema. Low methemoglobin levels may result in headache, weakness, and dyspnea. High methemoglobin levels may result in stupor, respiratory depression, and chocolate colored blood from lack of

oxygenation.
CHRONIC EXPOSURE- Prolonged and repeated exposure may cause heart and lung damage and pulmonary edema with possible coma and death.

SKIN CONTACT:
CHLOROPICRIN:
CORROSIVE/METHEMOGLOBIN FORMER.
ACUTE EXPOSURE- May cause irritation, redness, pain and skin burns. It is absorbed through the skin and may result in methemoglobinemia. Low methemoglobin levels may result in headache, weakness, and dyspnea. High methemoglobin levels may result in stupor, respiratory depression, and chocolate colored blood from lack of oxygenation.
CHRONIC EXPOSURE- Prolonged and repeated exposure may cause dermatitis and skin burns.

EYE CONTACT:
CHLOROPICRIN:
CORROSIVE/LACRIMATOR.
ACUTE EXPOSURE- May cause irritation, redness, pain, lacrimation, blurred vision and corneal damage.
CHRONIC EXPOSURE- May cause corneal damage and conjunctivitis.

INGESTION:
CHLOROPICRIN:
CORROSIVE/METHEMOGLOBIN FORMER/TOXIC.
ACUTE EXPOSURE- May cause irritation, sore throat, coughing, labored breathing, dizziness, nausea, vomiting, cyanosis, and faintness. Ingestion of liquid can cause severe gastroenteritis. Low methemoglobin levels may result in headache, weakness, and dyspnea. High methemoglobin levels may result in stupor, respiratory depression, and chocolate colored blood from lack of oxygenation.
CHRONIC EXPOSURE- May cause heart and lung damage.

SECTION 12 ECOLOGICAL INFORMATION

ENVIRONMENTAL IMPACT RATING (0-4): no data available

ACUTE AQUATIC TOXICITY: no data available

DEGRADABILITY: no data available

LOG BIOCONCENTRATION FACTOR (BCF): no data available

LOG OCTANOL/WATER PARTITION COEFFICIENT: no data available

SECTION 13 DISPOSAL CONSIDERATIONS

Observe all federal, state and local regulations when disposing of this substance.

SECTION 14 TRANSPORT INFORMATION

U.S. DEPARTMENT OF TRANSPORTATION SHIPPING NAME-ID NUMBER, 49 CFR 172.101:
Chloropicrin-UN 1580

U.S. DEPARTMENT OF TRANSPORTATION HAZARD CLASS OR DIVISION, 49 CFR 172.101:
6.1 - Poisonous materials

U.S. DEPARTMENT OF TRANSPORTATION PACKING GROUP, 49 CFR 172.101:
PG I

U.S. DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS, 49 CFR 172.101 AND SUBPART E:
Poison

U.S. DEPARTMENT OF TRANSPORTATION PACKAGING AUTHORIZATIONS:
EXCEPTIONS: None
NON-BULK PACKAGING: 49 CFR 173.227
BULK PACKAGING: 49 CFR 173.244

U.S. DEPARTMENT OF TRANSPORTATION QUANTITY LIMITATIONS 49 CFR 172.101:
PASSENGER AIRCRAFT OR RAILCAR: Forbidden
CARGO AIRCRAFT ONLY: Forbidden

SECTION 15 REGULATORY INFORMATION

TSCA INVENTORY STATUS: Y

CERCLA SECTION 103 (40CFR302.4):	N
SARA SECTION 302 (40CFR355.30):	N
SARA SECTION 304 (40CFR355.40):	N
SARA SECTION 313 (40CFR372.65):	Y
CHLOROPICRIN	
OSHA PROCESS SAFETY (29CFR1910.119):	Y
CHLOROPICRIN	500 pounds TQ
CALIFORNIA PROPOSITION 65:	N

SARA HAZARD CATEGORIES, SARA SECTIONS 311/312 (40 CFR 370.21)

ACUTE HAZARD:	Y
CHRONIC HAZARD:	N
FIRE HAZARD:	N
REACTIVITY HAZARD:	Y
SUDDEN RELEASE HAZARD:	Y

SECTION 16 OTHER INFORMATION

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OHS04770

SECTION 1 CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

MDL INFORMATION SYSTEMS, INC.
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1-510-895-1313

FOR EMERGENCY SOURCE INFORMATION
CONTACT: 1-615-366-2000 USA

CAS NUMBER: 67-66-3
RTECS NUMBER: FS9100000

SUBSTANCE: CHLOROFORM

TRADE NAMES/SYNONYMS:
TRICHLOROMETHANE; METHANE TRICHLORIDE; R 20; FREON 20; METHANE, TRICHLORO-; METHYL TRICHLORIDE; TRICHLOROFORM; R 20 (REFRIGERANT); METHENYL TRICHLORIDE; RCRA U044; UN 1888; STCC 4940310; CHCL3; OHS04770

CHEMICAL FAMILY:
Halogen compound, aliphatic

CREATION DATE: 10/01/84 REVISION DATE: 06/04/96

SECTION 2 COMPOSITION, INFORMATION ON INGREDIENTS

COMPONENT : CHLOROFORM
CAS NUMBER: 67-66-3
PERCENTAGE: >99

OTHER CONTAMINANTS: MAY CONTAIN TRACES OF A STABILIZER.

SECTION 3 HAZARDS IDENTIFICATION

NFPA RATINGS (SCALE 0-4): HEALTH=2 FIRE=0 REACTIVITY=0

EMERGENCY OVERVIEW:
Clear, colorless, heavy, volatile liquid with a sweet taste and odor.

Suspect cancer hazard (contains material which can cause cancer in animals). Risk of cancer depends on duration and level of contact. Causes respiratory tract, skin, and eye irritation. May damage the liver and the kidneys. May affect the central nervous system.

Avoid breathing vapor or mist. Avoid contact with eyes, skin and clothing. Keep container tightly closed. Wash thoroughly after handling. Use only with

adequate ventilation.

POTENTIAL HEALTH EFFECTS:
INHALATION:
SHORT TERM EFFECTS: May cause irritation. Additional effects may include nausea, vomiting, low blood pressure, irregular heartbeat, headache, drowsiness, drunkenness, fainting, disorientation, numbness, dilated pupils, convulsions and coma.
LONG TERM EFFECTS: In addition to effects from short term exposure, digestive disorders, tingling sensation, twitching, loss of memory, blurred vision, liver enlargement and liver and kidney damage may occur.
SKIN CONTACT:
SHORT TERM EFFECTS: May cause irritation.
LONG TERM EFFECTS: Same effects as short term exposure.
EYE CONTACT:
SHORT TERM EFFECTS: May cause irritation. Additional effects may include tearing and numbness.
LONG TERM EFFECTS: Same effects as short term exposure.
INGESTION:
SHORT TERM EFFECTS: May cause nausea, vomiting, diarrhea, blood in the urine, difficulty breathing, low blood pressure, drunkenness, dilated pupils and bluish skin color.
LONG TERM EFFECTS: In addition to effects from short term exposure, liver and kidney damage may occur. May also cause cancer.
ADDITIONAL DATA: Drinking alcohol may worsen the effects.

CARCINOGEN STATUS:
OSHA: N
NTP: Y
IARC: Y

SECTION 4 FIRST AID MEASURES

INHALATION:
FIRST AID- Remove from exposure area to fresh air immediately. Perform artificial respiration if necessary. Keep person warm and at rest. Treat symptomatically and supportively. Get medical attention immediately.

SKIN CONTACT:
FIRST AID- Remove contaminated clothing and shoes immediately. Wash with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). Get medical attention immediately.

EYE CONTACT:
FIRST AID- Wash eyes immediately with large amounts of water or normal saline, occasionally lifting upper and lower lids, until no evidence of chemical

remains (at least 15-20 minutes). Get medical attention immediately.

INGESTION:
FIRST AID- If vomiting occurs, keep head lower than hips to help prevent aspiration. Treat symptomatically and supportively. Get medical attention if needed.

NOTE TO PHYSICIAN
ANTIDOTE:
No specific antidote. Treat symptomatically and supportively.

SECTION 5 FIRE FIGHTING MEASURES

FIRE AND EXPLOSION HAZARD:
Negligible fire hazard when exposed to heat or flame.

EXTINGUISHING MEDIA:
Dry chemical, water spray or regular foam
(1993 Emergency Response Guidebook, RSPA P 5800.6).

For larger fires, use water spray, fog or regular foam
(1993 Emergency Response Guidebook, RSPA P 5800.6).

FIREFIGHTING:
Move container from fire area if you can do it without risk. Fight fire from maximum distance. Stay away from ends of tanks. Dike fire-control water for later disposal; do not scatter the material (1993 Emergency Response Guidebook, RSPA P 5800.6, Guide Page 55).

Extinguish using agents suitable for type of fire. Avoid breathing vapors or dusts, keep upwind.

FLASH POINT: no data available
LOWER FLAMMABLE LIMIT: no data available
UPPER FLAMMABLE LIMIT: no data available
AUTOIGNITION: >1832 F (>1000 C)

HAZARDOUS COMBUSTION PRODUCTS:
Thermal decomposition may release toxic or corrosive oxides of chlorine and carbon, phosgene, chlorine gas and hydrogen chloride.

SECTION 6 ACCIDENTAL RELEASE MEASURES

OCCUPATIONAL SPILL:
Do not touch spilled material. Stop leak if you can do it without risk. Use water spray to reduce vapors. For small spills, take up with sand or other absorbent material and place into containers for later disposal. For small

dry spills, with a clean shovel place material into clean, dry containers and cover. Move containers from spill area. For larger spills, dike far ahead of spill for later disposal. Keep unnecessary people away. Isolate hazard area and deny entry. Ventilate closed spaces before entering.

Reportable Quantity (RQ):
The Superfund Amendments and Reauthorization Act (SARA) Section 304 requires that a release equal to or greater than the reportable quantity established for that substance be immediately reported to the local emergency planning committee and the state emergency response commission (40 CFR 355.40). If the release of this substance is reportable under CERCLA Section 103, the National Response Center must be notified immediately at (800) 424-8802 or (202) 426-2675 in the metropolitan Washington, D.C. area (40 CFR 302.6).

SOIL SPILL:
Dig a holding area such as a pit, pond or lagoon to contain spill and dike surface flow using barrier of soil, sandbags, foamed polyurethane or foamed concrete. Absorb liquid mass with fly ash or cement powder.

Immobilize spill with universal gelling agent.

AIR SPILL:
Combustion products include corrosive or toxic vapors.

WATER SPILL:
Trap spilled material at bottom in deep water pockets, excavated holding areas or within sand bag barriers.

Use suction hoses to remove trapped spill material.

Use mechanical dredges or lifts to extract immobilized masses of pollution and precipitates.

If dissolved, at a concentration of 10 ppm or greater, apply activated carbon at ten times the amount that has been spilled.

The California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65) prohibits contaminating any known source of drinking water with substances known to cause cancer and/or reproductive toxicity.

SECTION 7 HANDLING AND STORAGE

Observe all federal, state and local regulations when storing this substance.

Threshold Planning Quantity (TPQ):
The Superfund Amendments and Reauthorization Act (SARA) Section 302 requires that each facility where any extremely hazardous substance is present in a quantity equal to or greater than the TPQ established for that substance

notify the state emergency response commission for the state in which it is located. Section 303 of SARA requires these facilities to participate in local emergency response planning (40 CFR 355.30).

Store in a cool, dry, well-ventilated location. Separate from strong alkalis (NFPA 49, Hazardous Chemicals Data, 1975).

Store away from incompatible substances.

Keep container tightly closed. Protect from exposure to air or light.

SECTION 8 EXPOSURE CONTROLS, PERSONAL PROTECTION

EXPOSURE LIMITS:
CHLOROFORM:
50 ppm (240 mg/m3) OSHA ceiling
2 ppm (9.78 mg/m3) OSHA TWA (vacated by 58 FR 35338, June 30, 1993)
10 ppm (49 mg/m3) ACGIH TWA
ACGIH A2-Suspected Human Carcinogen (Notice of Intended Changes 1995-96)
2 ppm (9.78 mg/m3) NIOSH recommended 60 minute STEL
10 ppm (49 mg/m3) DFG MAK TWA;
20 ppm (98 mg/m3) DFG MAK 30 minute peak, average value, 4 times/shift

Measurement method: Charcoal tube; carbon disulfide; gas chromatography with flame ionization detection; (NIOSH III # 1003, Halogenated hydrocarbons).

10,000 pounds SARA Section 302 Threshold Planning Quantity
5000 pounds SARA Section 304 Reportable Quantity
10 pounds CERCLA Section 103 Reportable Quantity
Subject to SARA Section 313 Annual Toxic Chemical Release Reporting
Subject to California Proposition 65 cancer and/or reproductive toxicity warning and release requirements- (October 1, 1987)

VENTILATION:
Provide local exhaust or process enclosure ventilation to meet published exposure limits.

EYE PROTECTION:
Employee must wear splash-proof or dust-resistant safety goggles and a faceshield to prevent contact with this substance.

Emergency wash facilities:
Where there is any possibility that an employee's eyes and/or skin may be exposed to this substance, the employer should provide an eye wash fountain and quick drench shower within the immediate work area for emergency use.

CLOTHING:
Employee must wear appropriate protective (impervious) clothing and equipment

to prevent repeated or prolonged skin contact with this substance.

GLOVES:
Employee must wear appropriate protective gloves to prevent contact with this substance.

RESPIRATOR:
The following respirators and maximum use concentrations are recommendations by the U.S. Department of Health and Human Services, NIOSH Pocket Guide to Chemical Hazards; NIOSH criteria documents or by the U.S. Department of Labor, 29 CFR 1910 Subpart Z.
The specific respirator selected must be based on contamination levels found in the work place, must not exceed the working limits of the respirator and be jointly approved by the National Institute for Occupational Safety and Health and the Mine Safety and Health Administration (NIOSH-MSHA).

CHLOROFORM:
At any detectable concentration:
Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive pressure-mode.
Any supplied-air respirator with a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

Escape- Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted organic vapor canister.
Any appropriate escape-type, self-contained breathing apparatus.

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:

Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode.

Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

DESCRIPTION: Clear, colorless, heavy, volatile liquid with a sweet taste and odor.
MOLECULAR WEIGHT: 119.38
MOLECULAR FORMULA: C-H-CL3
BOILING POINT: 143 F (62 C)
FREEZING POINT: -82 F (-64 C)
VAPOR PRESSURE: 160 mmHg @ 20 C

VAPOR DENSITY: 4.12
SPECIFIC GRAVITY: 1.4832
WATER SOLUBILITY: 0.82% @ 20 C
VOLATILITY: 100%
[illegible]: no data available
ODOR THRESHOLD: 200 ppm
EVAPORATION RATE: (butyl acetate=1) 11.6
VISCOSITY: 56.3 cP @ 20 C
SOLVENT SOLUBILITY: Soluble in alcohol, ether, acetone, benzene, ligroin, solvent naphtha, petroleum ether, carbon tetrachloride, carbon disulfide, oils, other organic solvents.

SECTION 10 STABILITY AND REACTIVITY

REACTIVITY:
Stable under normal temperatures and pressures.

CONDITIONS TO AVOID:
May burn but does not ignite readily. Containers may explode in heat of fire.

INCOMPATIBILITIES:
CHLOROFORM:
ALUMINUM (POWDERED): Explosion on contact.
BIS(DIMETHYLAMINO)DIMETHYLSTANNANE: Explosion when heated.
DINITROGEN TETRAOXIDE: Explosive mixture.
DISILANE: Vigorous incandescent reaction.
FLUORINE: Explosive reaction.
KETONES + ALKALIES: Vigorous exothermic reaction.
LITHIUM: Forms shock-sensitive mixture.
MAGNESIUM (POWDER): Explodes on contact.
METALS + WATER: May be attacked.
METHANOL + ALKALIES: Exothermic reaction.
NITROMETHANE: Forms explosive mixture.
PERCHLORIC ACID + PHOSPHOROUS PENTOXIDE: Violent explosion.
PLASTICS, RUBBER, COATINGS: May be attacked.
POTASSIUM: Explosive reaction.
POTASSIUM TERT-BUTOXIDE (VAPOR): Ignites on contact.
SODIUM: Explosive reaction.
SODIUM METHOXIDE: Incompatible.
TRIISOPROPYLPHOSPHINE: Vigorous reaction.

HAZARDOUS DECOMPOSITION:
Thermal decomposition may release toxic or corrosive oxides of chlorine and carbon, phosgene, chlorine gas and hydrogen chloride.

POLYMERIZATION:
Hazardous polymerization has not been reported to occur under normal temperatures and pressures.

SECTION 11 TOXICOLOGICAL INFORMATION

CHLOROFORM:

IRRITATION DATA: 10 mg/24 hours open skin-rabbit mild; 500 mg/24 hours skin-rabbit mild; 148 mg eye-rabbit; 20 mg/24 hours eye-rabbit moderate.

TOXICITY DATA: 25000 ppm/5 minutes inhalation-human LCLo; 10 mg/m3/1 year inhalation-human TCLo; 5000 mg/m3/7 minutes inhalation-human TCLo; 47702 mg/m3/4 hours inhalation-rat LC50; 50 ppm/7 hours/26 weeks-intermittent inhalation-rat TCLo; 10 ppm/6 hours/7 days-intermittent inhalation-rat TCLo; 300 ppm/6 hours/7 days-intermittent inhalation-rat TCLo; 23 gm/m3/56 minutes inhalation-mouse LCLo; 12 ppm/6 hours/13 weeks-intermittent inhalation-mouse TCLo; 100 ppm/6 hours/7 days-intermittent inhalation-mouse TCLo; 59 gm/m3 inhalation-rabbit LCLo; 35 gm/m3/4 hours inhalation-cat LCLo; 100 gm/m3 inhalation-dog LCLo; 20000 ppm/2 hours inhalation-guinea pig LCLo; 85 ppm/7 hours/26 weeks-intermittent inhalation-guinea pig TCLo; 25 ppm/7 hours/26 weeks-intermittent inhalation-dog TCLo; 85 ppm/7 hours/26 weeks-intermittent inhalation-rabbit TCLo; 25000 ppm/5 minutes inhalation-mammal LCLo; >20 gm/kg skin-rabbit LD50; >4000 mg/kg skin-rabbit LD50 (Dow MSDS); 2514 mg/kg oral-man LDLo; 908 mg/kg oral-rat LD50; 36 mg/kg oral-mouse LD50; 1 gm/kg oral-dog LDLo; 500 mg/kg oral-rabbit LDLo; 820 mg/kg oral-guinea pig LD50; 7560 mg/kg/21 days-intermittent oral-rat TDLo; 5 mg/kg/10 days-intermittent oral-rat TDLo; 1750 mg/kg/14 days-continuous oral-mouse TD; 800 mg/kg subcutaneous-rabbit LDLo; 704 mg/kg subcutaneous-mouse LD50; 75 mg/kg intravenous-dog LDLo; 894 mg/kg intraperitoneal-rat LD50; 623 mg/kg intraperitoneal-mouse LD50; 1 gm/kg intraperitoneal-dog LD50; 546 mg/kg unreported-man LDLo; mutagenic data (RTECS); reproductive effects data (RTECS); tumorigenic data (RTECS).

CARCINOGEN STATUS: Anticipated Human Carcinogen (NTP); Human Inadequate Evidence, Animal Sufficient Evidence (IARC Group-2B). Chloroform produced benign and malignant tumors of the liver and kidney in mice following oral gavage. Administration to rats by gavage or in drinking-water increased the incidences of kidney and thyroid tumors and of neoplastic nodules of the liver.

LOCAL EFFECTS: Irritant- inhalation, skin, eye.

ACUTE TOXICITY LEVEL: Moderately toxic by ingestion; slightly toxic by inhalation and dermal absorption.

TARGET EFFECTS: Central nervous system depressant; hepatotoxin, nephrotoxin. Poisoning may also affect the heart.

AT INCREASED RISK FROM EXPOSURE: Alcoholics and persons with chronic skin, eye, liver, kidney, heart or respiratory disorders.

ADDITIONAL DATA: Alcohol may enhance the toxic effects. Use of, or exposure to, steroids, polybrominated biphenyls, acetone, or chlordecone may enhance the toxic effects. May be excreted in breast milk. Stimulants such as epinephrine may induce ventricular fibrillation.

HEALTH EFFECTS
INHALATION:
CHLOROFORM:
IRRITANT/NARCOTIC/HEPATOTOXIN/NEPHROTOXIN.
[redacted] ppm Immediately Dangerous to Life or Health.
ACUTE EXPOSURE- May cause irritation of the upper respiratory tract. Central nervous system depression may be preceded by excitation and inebriation. 1,000-2,000 ppm may cause dizziness, headache, fatigue, salivation, and nausea; 4,000 ppm may cause vomiting, serious disorientation, and a fainting feeling; 14,000-16,000 ppm may cause anesthesia and rapid loss of consciousness; more than 20,000 ppm may cause respiratory failure, cardiac arrhythmias, and death. Other symptoms may include a feeling of warmth, malaise, drowsiness, mydriasis with diminished light reflex, toxemia, loss of tendon reflexes, stupor, convulsions, coma and hypotension. Fatty changes and centrilobular necrosis of the liver and fatty degenerative changes of the kidney and heart may occur. If death does not occur immediately from respiratory arrest or ventricular fibrillation, it may occur later from liver and kidney damage.
CHRONIC EXPOSURE- Repeated exposure to 77-237 ppm has caused lassitude, dullness, urinary frequency, and gastrointestinal disturbances. Other reported symptoms include dry mouth, thirst, malaise, anorexia, headache, depression, confusion, weakness, blurred vision, paresthesias, loss of sense of balance, memory loss, tremors, anemia, kidney damage, and fatty degeneration of the liver. 17 of 68 workers exposed to 10-200 ppm for 1-4 years exhibited hepatomegaly and increased susceptibility to viral hepatitis. High doses resulted in lesions in the liver and nasal passages of mice and histologic changes, necrosis and cell proliferation in the kidneys of male mice. Exposure of rats on days 6-15 of gestation caused a high rate of resorptions, retarded fetal development, decreased fetal body measurements, and a low incidence of acaudate fetuses with imperforate anus. Mice exposed on days 8-15 of gestation had offspring with a significant increase of cleft palate. One noncorroborated study reports abnormal spermatozoa in mice exposed to levels above the TLV.

SKIN CONTACT:
CHLOROFORM:
IRRITANT.
ACUTE EXPOSURE- May cause irritation with inflammation, destruction of the epithelium, and prurulent blebs. Application to rabbit skin for 24 hours caused hyperemia and moderate necrosis. Some absorption occurred resulting in weight loss and degenerative kidney changes, however doses as high as 3980 mg/kg were survived.
CHRONIC EXPOSURE- Repeated or prolonged exposure may cause dermatitis with drying, cracking, and redness. If sufficient amounts are absorbed, systemic effects may occur.

EYE CONTACT:
CHLOROFORM:

IRRITANT.
ACUTE EXPOSURE- High vapor concentrations may cause stinging, irritation, and blepharospasm. Contact with the liquid may also cause burning pain, lacrimation, and redness. The corneal epithelium may be injured and partially lost, however, the eyes return to normal in 1-3 days. Long exposure of the cornea during general anesthesia has caused persistent injury.
CHRONIC EXPOSURE- Repeated or prolonged contact with irritants may cause conjunctivitis.

INGESTION:
CHLOROFORM:
NARCOTIC/HEPATOTOXIN/NEPHROTOXIN/CARCINOGEN.
ACUTE EXPOSURE- May cause burning of the mouth, throat, esophagus, and stomach, nausea, vomiting, diarrhea, abdominal and substernal pain, cold, clammy skin, cyanosis of the extremities and face, muscle cramps, mydriasis, hypotension, peripheral vasodilation, irregular respiration, respiratory failure, unconsciousness, and liver damage. The mean lethal dose in humans is about 1 ounce. Aspiration may occur and result in chemical pneumonitis. 250 mg/kg caused depression, profound sleep, dyspnea, anorexia, hematuria, and liver and kidney changes in rats.
CHRONIC EXPOSURE- Repeated ingestion may cause liver and kidney damage. In feeding studies, there was an increased incidence of benign and malignant tumors of the liver and kidneys in mice and of tumors of the kidney and thyroid and neoplastic nodules in the liver in rats. Reproductive effects have been reported in animals.

SECTION 12 ECOLOGICAL INFORMATION

ENVIRONMENTAL IMPACT RATING (0-4): no data available

ACUTE AQUATIC TOXICITY: no data available

DEGRADABILITY: no data available

LOG BIOCONCENTRATION FACTOR (BCF): no data available

LOG OCTANOL/WATER PARTITION COEFFICIENT: no data available

SECTION 13 DISPOSAL CONSIDERATIONS

Observe all federal, state and local regulations when disposing of this substance.

Disposal must be in accordance with standards applicable to generators of hazardous waste, 40CFR 262. EPA hazardous waste number U044.

Chloroform - Regulatory level: 6.0 mg/l (TCLP-40 CFR 261 Appendix II) materials which contain the above substance at or above the TCLP regulatory level meet the EPA toxicity characteristic, and must be disposed of in accordance with 40 CFR part 262. EPA Hazardous Waste Number D022.

US EPA RCRA Hazardous Waste Number: RCRA U044

SECTION 14 TRANSPORT INFORMATION

U.S. DEPARTMENT OF TRANSPORTATION SHIPPING NAME-ID NUMBER, 49 CFR 172.101:
Chloroform-UN 1888

U.S. DEPARTMENT OF TRANSPORTATION HAZARD CLASS OR DIVISION, 49 CFR 172.101:
6.1 - Poisonous materials

FOR DOMESTIC TRANSPORTATION:

U.S. DEPARTMENT OF TRANSPORTATION PACKING GROUP, 49 CFR 172.101:
PG III

U.S. DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS, 49 CFR 172.101 AND SUBPART E:
Keep away from food

U.S. DEPARTMENT OF TRANSPORTATION PACKAGING AUTHORIZATIONS:
EXCEPTIONS: 49 CFR 173.150
NON-BULK PACKAGING: 49 CFR 173.203
BULK PACKAGING: 49 CFR 173.241

U.S. DEPARTMENT OF TRANSPORTATION QUANTITY LIMITATIONS 49 CFR 172.101:
PASSENGER AIRCRAFT OR RAILCAR: 5 L
CARGO AIRCRAFT ONLY: 60 L

FOR INTERNATIONAL TRANSPORTATION:

U.S. DEPARTMENT OF TRANSPORTATION PACKING GROUP, 49 CFR 172.101:
PG II

U.S. DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS, 49 CFR 172.101 AND SUBPART E:
Poison

U.S. DEPARTMENT OF TRANSPORTATION PACKAGING AUTHORIZATIONS:
EXCEPTIONS: None
NON-BULK PACKAGING: 49 CFR 173.202
BULK PACKAGING: 49 CFR 173.241

U.S. DEPARTMENT OF TRANSPORTATION QUANTITY LIMITATIONS 49 CFR 172.101:

PASSENGER AIRCRAFT OR RAILCAR: 5 L
CARGO AIRCRAFT ONLY: 60 L

SECTION 15 REGULATORY INFORMATION

TSCA INVENTORY STATUS: Y

CERCLA SECTION 103 (40CFR302.4):	Y	
CHLOROFORM		10 pounds RQ
SARA SECTION 302 (40CFR355.30):	Y	
CHLOROFORM		10,000 pounds TPQ
SARA SECTION 304 (40CFR355.40):	Y	
CHLOROFORM		5000 pounds RQ
SARA SECTION 313 (40CFR372.65):	Y	
CHLOROFORM		
OSHA PROCESS SAFETY (29CFR1910.119):	N	
CALIFORNIA PROPOSITION 65:	Y	
CHLOROFORM		

SARA HAZARD CATEGORIES, SARA SECTIONS 311/312 (40 CFR 370.21)

ACUTE HAZARD:	Y
CHRONIC HAZARD:	Y
FIRE HAZARD:	N
REACTIVITY HAZARD:	N
SUDDEN RELEASE HAZARD:	N

SECTION 16 OTHER INFORMATION

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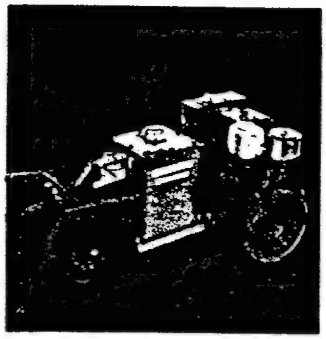
Attachment 2

OPERATING INSTRUCTIONS AND SAFETY NOTICE FOR LITTLE BEAVER HYDRAULIC EARTH DRILLS

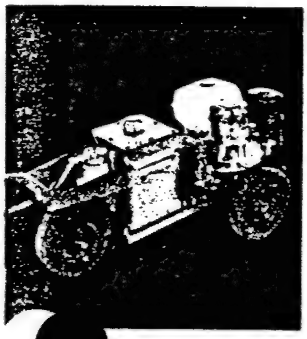
MODELS AVAILABLE

One Man Handle

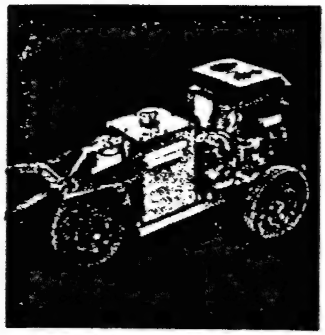
Two Man Handle



11 H.P. Briggs & Stratton Industrial/Commercial engine



V Honda engine



11 H.P. Wisconsin Robin engine

LITTLE BEAVER, INC.
P.O. Box 840
Livingston, Texas 77351
Phone: (409) 327-3121
FAX: (409) 327-4025

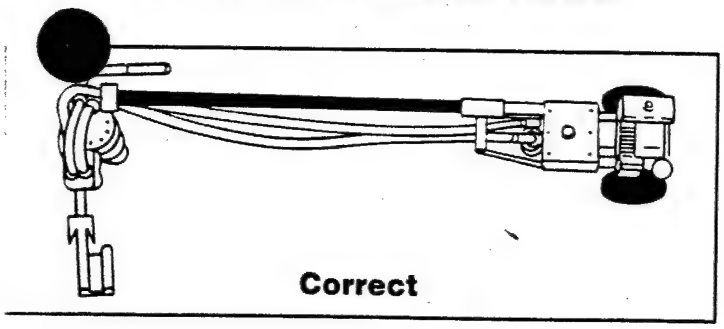
OPERATING INSTRUCTIONS for Hydraulic Earth Drills

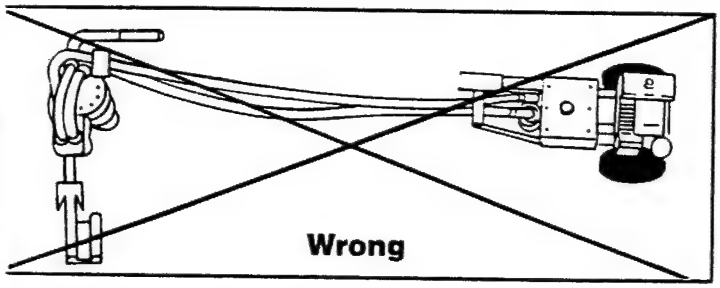
Models PS8, PS10, or PS11 with one man or two man handle

LITTLE BEAVER, INC.

Operating Instructions

ALWAYS USE TORQUE TUBE





TORQUE TUBE ASSEMBLY

The torque tube consists of two parts. Part #1 is 60" long with a 1-½" square fitting on one end. Part #2 is 29" long with a 1-¼" square fitting on one end. To assemble, slide part #2 into part #1 so that the square fittings are on opposite ends. Attach the larger end of the torque tube to the power source bracket. Attach the other end to the handle. Be sure to align the snap button with the hole provided and check to be sure the snap buttons are securely snapped into place.

BEFORE STARTING THE ENGINE

Be sure that :

1. The torque tube is properly attached
2. There is no auger connected to the handle
3. The Quick Disconnect fittings are correctly coupled.
4. The Torque Tube has engaged the Kill Switch at the Power Source.

TO START THE ENGINE

Set the choke lever to the "ON" position and pull the starter rope. The engine should start after 2 or 3 pulls. Set the choke lever to the "OFF" position and allow the engine to warm-up for 2 or 3 minutes.

AFTER THE ENGINE HAS WARMED UP

Insert the auger into the drive adaptor on the bottom of the handle. Make sure the snap button and hole provided in the adaptor are aligned and the button snaps securely into place. Hold the handle so your left index finger and thumb can operate the throttle (pull with the index finger for forward rotation, push with the thumb for reverse.) NOTE: ONLY use reverse to free the auger if it becomes lodged in the ground. Grasp the right handle bar with your right hand. Stand so the auger is straight up-and-down and is properly positioned to dig your hole. making certain your feet are well clear of the auger. Note the safety instructions in this manual and on the machine's decals.

IMPORTANT

Keep your back as vertical as possible by bending your legs, as required, during the operating and lifting procedure.

ONE-MAN HANDLE

Always keep the leg pad against leg to maintain safe and stable control during operation.

TWO-MAN HANDLE

The operator controlling the throttle lever must alert the other operator prior to engaging the earth drill to ensure readiness. Both operators must distribute even pressure on the auger, as required, to maintain uniform drilling.

OPERATION

NEVER Drill holes where there is a possibility of underground power cables or other hazards.

MAKE certain everyone is clear before operating the machine.

KEEP hands, feet and clothing away from moving parts while engine is running.

Start The Auger Turning By pulling the throttle lever in completely. Always allow the auger to turn at full speed and let it cut its way into the soil.

Important: When digging in soft soil, hold up slightly on auger. In hard pan, apply pressure, but not enough to stall the auger or slow it down significantly. The auger works best when it turns at full speed.

If The Auger Stalls repeatedly or slows down significantly; stop the auger by releasing throttle lever, slightly lift up on auger, start auger by pulling throttle lever, and allow the auger to turn at full speed while slowly lowering it to bottom of hole.

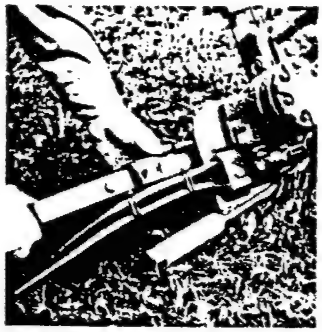
When the desired depth is reached, stop the auger by releasing the throttle lever. Then pull the auger completely out of the hole.

NEVER Remove auger from hole while auger is turning.

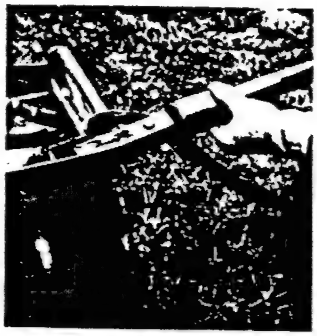
How to operate Earth Drill

1 Connect handle tc power source using quick disconnect fittings.

2 Connect male and female ends of torque tube together.



3 Snap male end of torque tube into connector at handle.



4 Snap female end of torque tube into connector on power source.

5 Starting position: Choke ine, then pull starter rope. e: engine should always run at full speed.

6 Attach auger to auger adaptor.

7 For safety, always keep leg pad against leg while digging.

8 When hole is complete, stop auger and pull out for clean hole.

9 For greater depth: unsnap auger from auger adaptor.

10 Snap extension onto auger.

11 Continue digging with auger and extension.

12 Remove handle, then remove auger and extension from hole.

TROUBLE	CAUSE
Engine will not start	1) Torque tube is not connected at power source 2) Engine stop switch is in "off" or "O" position 3) Low fuel level in gas tank 4) Low oil level in "Oil Guard" or "Oil Alert" equipped engines 5) Spark plug fouled
Cannot connect or disconnect auger	1) Foreign matter clogging auger adaptor 2) Spring and button in top of auger is bent or broken 3) Auger adaptor is bent
Auger turns too slowly and will not dig	1) Too much downward pressure or binding on side of hole. Hold back if necessary to allow auger to turn at full speed. 2) Bent linkage between control lever and valve. With engine off, ensure that neither lever touches handle bar when moved to full forward or reverse position.
Auger turns but will not dig	1) Foreign matter collected around point 2) Point or blade is dull 3) Wrong blade type for soil condition. Contact your dealer or factory for Little Beaver carbide blade
er with extension will not dig	1) Auger or extension bent or running out of line 2) Number of extensions exceeds capacity of machine
Hydraulic oil and/or hoses overheats	1) It is normal for the hoses and reservoir to be warm to the touch. If it is very hot, consult your dealer or factory.
Auger turns when engine idles	1) Valve or linkage is binding. Do not use. Consult your dealer or factory
Problems not listed in table	1) Consult your dealer or factory

SAFETY PRECAUTIONS

DANGER: Failure to observe safety instructions and reasonable safety practices can cause Property Damage, Serious Bodily Injury and/or Death. BE CAREFUL!! WATCH OUT FOR BYSTANDERS!!

DANGER: NEVER drill holes where there is a possibility of underground power cables or other hazards.

WARNING: Augers are not to be used as anchoring devices.

CAUTION:

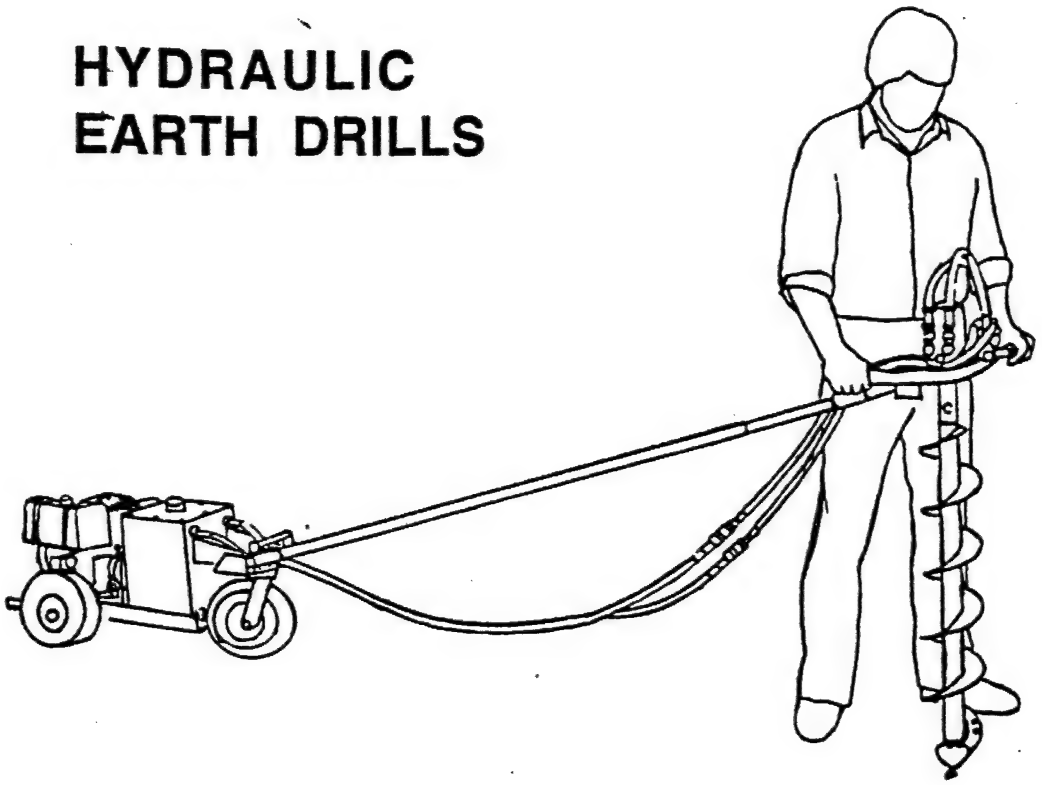
1. NEVER Operate drill without correctly installing torque tube.
2. NEVER Remove auger from hole while auger is turning.
3. NEVER Operate auger at less than full throttle.
4. NEVER Operate drill with damaged auger or other damaged or missing parts.
5. KEEP Hands, Feet and Clothing away from moving parts while engine is running.
6. KEEP All safety shields and devices in place.
7. MAKE Certain everyone is clear before operating the machine.
8. KEEP leg pad against leg while drilling to maintain safe control.
9. WEAR SAFETY GLASSES.
10. KEEP Bystanders away from work area.
11. SHUT OFF Engine to adjust, service or clean the machine.

CAUTION: Escaping hydraulic fluid, under pressure, can have sufficient force to penetrate the skin, causing serious injury. Before disconnecting hydraulic lines, be sure to relieve pressure. Before applying pressure, be sure connections are tight and fittings, pipes and hoses are not damaged. Use a piece of cardboard or wood, rather than hands, to search for leaks.

KEEP all hydraulic lines away from moving parts.

LITTLE BEAVER

HYDRAULIC EARTH DRILLS



OPERATORS MANUAL
WITH
MAINTENANCE AND PARTS INFORMATION

LITTLE BEAVER, INC.

P.O. BOX 840 ● LIVINGSTON, TEXAS 77351
PHONE 409/327-3121 ● FAX 409/327-4025

MFG. BY: LB EQUIPMENT, INC. - LIVINGSTON, TEXAS USA

SAFETY INSTRUCTIONS

DANGER: Failure to observe safety instructions and reasonable safety practices can cause Property Damage, Serious Bodily Injury and/or Death. BE CAREFUL!! WATCH OUT FOR BYSTANDERS!!

DANGER: NEVER run engine inside building or enclosed area. Exhaust gases contain carbon monoxide, an odorless and deadly poison.

DANGER: NEVER drill holes where there is a possibility of underground power cables or other hazards. The exact location of underground services must be determined prior to drilling. Inadvertent severing of telephone, fiber optic or CATV transmission cable, or damage to sewer pipe is costly; RUPTURING OF GAS OR WATER LINES CAN CAUSE SERIOUS BODILY INJURY AND/OR DEATH. COMING INTO CONTACT WITH BURIED POWER LINES CAN CAUSE SERIOUS BODILY INJURY, SEVERE BURNS, AND/OR ELECTROCUTION. Call local utility companies or your local "One-Call" number at least 48 hours before digging and have underground utilities marked.

WARNING: Never use hands to search for leaks. Instead, use a piece of cardboard or wood. Escaping hydraulic fluid under pressure can have sufficient force to penetrate the skin, causing serious injury. Before disconnecting lines, be sure to relieve pressure. Before applying pressure, be sure connections are tight and fittings and hoses are not damaged.

WARNING: Augers are not to be used as anchoring devices.

CAUTION:

1. READ and understand this operator's manual and the operator's manual for the engine.
2. NEVER Operate drill without correctly installing torque tube.
3. NEVER Remove auger from hole while auger is turning.
4. NEVER Operate auger at less than full throttle.
5. NEVER Operate drill with damaged auger or other damaged or missing parts.
6. KEEP Hands, Feet and Clothing away from moving parts while engine is running.
7. KEEP All safety shields and devices in place.
8. MAKE Certain everyone is clear before operating the machine.
9. KEEP Leg pad against leg while drilling to maintain safe control.
10. WEAR SAFETY GLASSES.
11. KEEP Bystanders away from work area.
12. SHUT OFF Engine to adjust, service or clean the machine.

NOTICE

It is the responsibility of the contractor, owner and user to maintain and operate the Earth Drill in compliance with operating instructions provided. Observe all listed safety instructions and other reasonable safety practices. LB EQUIPMENT, INC. accepts no responsibility for damages to this machine, and other property damage and/or bodily injury due to careless or improper operations.

LB EQUIPMENT, INC. does not recommend or condone any modifications which would eliminate the torque tube.

LB EQUIPMENT, INC. does not recommend use of replacement hydraulic motors which would result in auger shaft torque greater than 400 ft.-lbs. If greater torque is required, please consult factory.

LB EQUIPMENT, INC. reserves the right to make changes in design and changes for improvements upon its product without imposing any obligation upon itself to install the same upon its products theretofore manufactured.

Your operators manual offers recommendations for prolonged and satisfactory service.

SPECIFICATIONS

11 HP Honda, 11 HP Briggs & Stratton OR 11 HP Wisconsin
6 GPM @ 2000 PSI
100 Micron Suction Screen
10 Micron Replaceable Return Line Filter
5 Gallon Hydraulic Reservoir

MAINTENANCE AND LUBRICATION INSTRUCTIONS

NOTE: All engines and hydraulic reservoirs are shipped WITHOUT oil.

ENGINE: The engine is shipped without oil or gasoline. Refer to the manufacturers instructions for proper procedures and recommended fluid.

HYDRAULIC FLUID AND FILTER: The hydraulic reservoir should be filled to the top of the sight gauge with AW 32 or ISO 32 hydraulic oil before attempting to start the engine. The hydraulic oil and return line filter (Part # 30280) must be kept clean at all times, and should be changed after the first 15 hours of operation. The filter and oil should be changed every three months or after100 hours of operation; whichever comes first.

NOTE: The hydraulic fluid and engine crankcase oil levels should be checked prior to each days use.

IMPORTANT: All nuts, fasteners, and fittings must be kept tightened. If the engine or tank mounting bolts are allowed to loosen, premature coupling and/or pump wear may result.

⚠ **CAUTION:** Escaping hydraulic fluid under pressure can have sufficient force to penetrate the skin, causing serious injury. Before disconnecting hydraulic lines, be sure to relieve pressure. Before applying pressure, be sure connections are tight and fittings, pipes and hoses are not damaged. Use a piece of cardboard or wood, rather than hands, to search for leaks. If injured by escaping fluid, see a doctor at once. Serious infection or reaction can develop if proper medical treatment is not administered immediately.

⚠ **KEEP** all hydraulic lines away from moving parts.

HYDRAULIC OIL LEAKAGE

If any hydraulic oil leakage is encountered, shut down the power source and relieve the hydraulic pressure by moving the throttle valve in both directions. Check and tighten the screw-on fittings on the end of each hose. If the leakage persists, it may be necessary to replace the associated hose assembly. If one of the Quick Disconnect fittings is the source of leakage, the seal or the quick disconnect coupling.should be replaced. If the throttle valve is leaking around the spool (shaft), you may replace the seal kit (Part # 30275-2).

NOTE: To obtain maximum performance from power source, minimum hose size recommended is 3/8".

HYDRAULIC HOSE ASSEMBLY REPLACEMENT

⚠ **WARNING:** For power source serial numbers from H-0001 through H-3252, do not exceed the following maximum hose assembly lengths. Longer hose assemblies may allow the torque tube to uncouple, causing serious personal injury.

If replacement hose assemblies are required, the maximum overall length of the pressure/return hose assembly on the handle is 36". The maximum overall length of the pressure hose assembly on the power source is 74 1/4" and the maximum overall length of the return hose assembly on the power source is 68".

EXCESSIVE HEATING

Excessive heating is caused by placing too much down pressure on the auger which causes the oil pressure to reach relief pressure. Oil flowing over the relief valve generates the heat.

DECAL LOCATION

The decals which are provided with your machine are shown at the rear of this manual. The decals shown should be in the locations as described. If any of the decals are missing or illegible, order replacement decal kit # 30181-D# and install before operating the machine.

WHEEL ASSEMBLY

Attach a wheel to each end of the rear axle using a 3/4" flat washer and securing with a 1/8" x 1" cotter key. Attach the front wheel to the swivel bracket using one 3/4" x 5-1/2" cap screw, two spacers, and one [illegible]" lock nut.

OPERATION

TORQUE TUBE ASSEMBLY

⚠ **WARNING:** Properly install torque tube to prevent serious injury from kick-back torque while drilling.

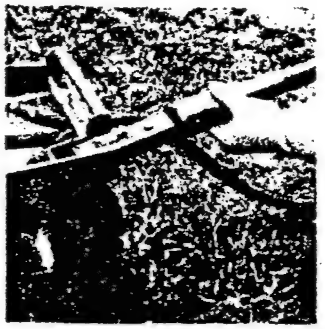


Figure 1

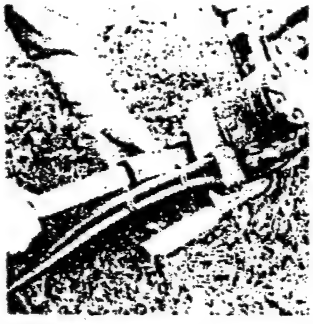


Figure 2

The torque tube consists of one end with a 1-1/2" square female fitting and a 1-1/4" square male fitting on the other end. Attach the larger female end of the torque tube to the power source bracket as shown in figure 1. Attach the other male end to the handle as shown in figure 2. Be sure to align the snap button with the mating hole provided and check to be sure the snap buttons are securely snapped into place.

BEFORE STARTING THE ENGINE, Be sure that:

⚠ **DANGER:** NEVER run engine inside building or enclosed area. Exhaust gases contain carbon monoxide, an odorless and deadly poison.

1.) Engine is properly prepared to Manufacturer's specifications. Note: Engines with "Oil Guard" protection must be filled with oil to full mark on dipstick or to point of overflowing to allow the engine to start.

2.) Hydraulic Reservoir is filled to top of sight gauge.

3.) The torque tube is properly attached.

4.) There is no auger connected to the handle.

5.) The Quick Disconnect fittings are correctly coupled.

6.) The Torque Tube has engaged the Kill Switch at the Power Source.

TO START THE ENGINE: Set the choke lever to the "ON" position and pull the starter rope. The engine should start after 2 or 3 pulls. Set the choke lever to the "OFF" position and allow the engine to warm-up for 2 or 3 minutes.

AFTER THE ENGINE HAS WARMED UP, Insert the auger into the drive adaptor on the bottom of the handle. Make sure the snap button and hole provided in the adaptor are aligned and the button snaps securely into place. Hold the handle so your left index finger and thumb can operate the throttle (pull with the index finger for forward rotation, push with the thumb for reverse). NOTE: ONLY use reverse to free the auger if it becomes lodged in the ground. Grasp the right handle bar with your right hand. Stand so the auger is straight up-and-down and is properly positioned to dig your hole (see figures 3 & 4). Note the safety instructions in this manual and on the machine's decals.

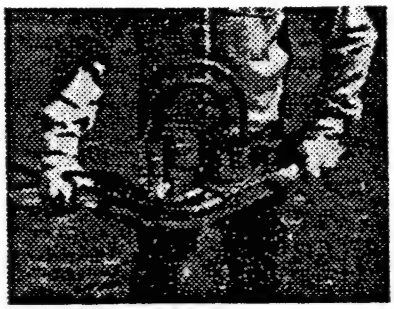


FIGURE 3

FIGURE 4

IMPORTANT: Keep the back as vertical as possible by bending the legs, as required, during the operating and lifting procedure.

ONE-MAN HANDLE

Always keep the leg pad against leg to maintain safe and stable control during operation.

TWO-MAN HANDLE

The operator controlling the throttle lever must alert the other operator prior to engaging the earth drill to ensure readiness. Both operators must distribute even pressure on the auger, as required, to maintain uniform drilling.

⚠ **DANGER:** NEVER drill holes where there is a possibility of underground power cables or other hazards. The exact location of underground services must be determined prior to drilling. Inadvertent severing of telephone, fiber optic or CATV transmission cable, or damage to sewer pipe is costly; RUPTURING OF GAS OR WATER LINES CAN CAUSE SERIOUS BODILY INJURY AND/OR DEATH. COMING INTO CONTACT WITH BURIED POWER LINES CAN CAUSE SERIOUS BODILY INJURY, SEVERE BURNS, AND/OR ELECTROCUTION. Call local utility companies or your local "One-Call" number at least 48 hours before digging and have underground utilities marked.

⚠ **MAKE** certain everyone is clear before operating the machine.

⚠ **KEEP** hands, feet and clothing away from moving parts while engine is running.

START THE AUGER TURNING By pulling the throttle lever in completely. Always allow the auger to turn at full speed and let it cut its way into the soil.

IMPORTANT: When digging in soft soil, hold up slightly on auger. In hard pan, apply pressure, but not enough to stall the auger or slow it down significantly. The auger works best when it turns at full speed.

IF THE AUGER STALLS repeatedly or slows down significantly; stop the auger by releasing throttle lever, slightly lift up on auger, start auger by pulling throttle lever, and allow the auger to turn at full speed while slowly lowering it to bottom of hole.

⚠ **NEVER** Remove auger from hole while auger is turning.

When the desired depth is reached, stop the auger by releasing the throttle lever. Then pull the auger completely out of the hole.

IMPORTANT: Keep the back as vertical as possible by bending the legs, as required, during the operation and lifting procedure.

AUGER EXTENSIONS

If greater hole depths are required, extensions may be used with the auger. After the auger has reached its maximum depth, stop the auger and disconnect the drive adaptor from the auger which remains in the hole. Connect the extension to the auger as shown in figure 5. Connect the drive adaptor to the extension and continue to dig the hole.

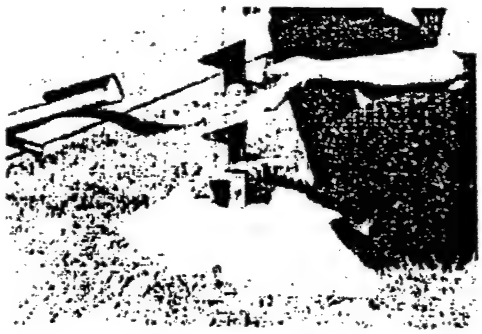


FIGURE 5

When the desired depth is reached, stop the auger and disconnect the drive adaptor from the extension then remove the extension(s) and auger from the hole.

⚠ When working with cutting blade, point and auger flighting; be careful not to be cut by sharp edges.

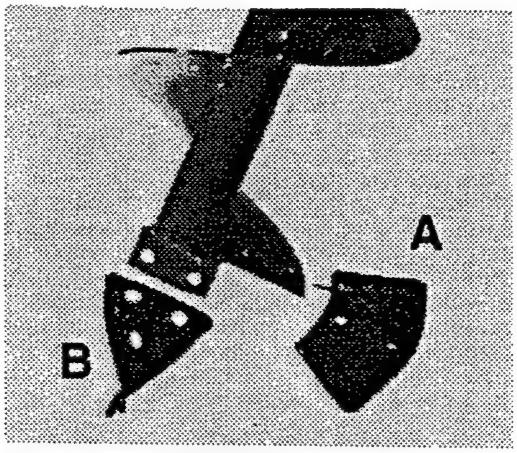


FIGURE 6

CUTTING BLADE

Check the cutting blade (Item A, Figure 6) on the auger frequently. If it becomes dull, it may be reversed to use the other cutting edge. If the outside of the blade wears even with the auger flighting, replace the blade or rebuild it with a hard surfacing rod. This is very important to reduce auger flighting wear and damage. The point (Item B, Figure 6) should be replaced when it loses its cutting shape.

ATTACHMENTS:

Several attachments are available for your LITTLE BEAVER Earth Drill; including both west and dry type horizontal boring kits and a drill chuck adaptor which allows you to use a wood bit. Refer to the specific operating instructions supplied with the attachment. If these become lost or misplaced, replacements may be obtained from the factory.

APPENDIX B
METHODS AND PROCEDURES

APPENDIX B-1

LAB PROCEDURES FOR SOIL pH: ASA METHOD 12-2.6

Determination of Soil pH
ASA 12-2.6

1.0 Purpose

This procedure provides a method for determination of soil pH using a glass electrode and pH meter.

2.0 Scope

Measure the pH of soil samples at all soil pH ranges.

3.0 Summary

A 5 g sample of soil is mixed with 5 mL water in a 28 g paper cup or a 50 mL beaker. Soils are stirred for 5 seconds and allowed to stand for 10 minutes. Electrodes are inserted into the supernatant and read pH immediately on a standardized pH meter.

4.0 References

McLean, E.O. 1982. Soil pH and Lime Requirement. Pages 199-224 in (A.L. Page, R.H. Miller, and D.R. Keeney, eds.) Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties. Agronomy Monographs no. 9 (2nd Edition).

5.0 Requirements

5.1 Prerequisites

Material Safety Data Sheets (MSDS) are available for standard pH buffers.

5.2 Apparatus/Equipment

pH meter equipped with glass electrodes (indicating and reference)

Pipettes

Paper cups, 28 g, or 50 mL beakers

Analytical balance capable of weighing to 0.01 g.

Glass or plastic rods for stirring.

5.3 Reagents and Standards

5.3.1 Reagents

Deionized water.

5.3.2 Standards

Standard pH buffers – pH 7 and 4.

6.0 Procedure

Set pH meter at pH 7 with a standard buffer solution pH 7 and set the manual temperature compensator at the temperature of the buffer. Check to see that the meter reads near pH 4 with a standard pH 4 buffer solution. If necessary, adjust the reading to pH 4 with the temperature compensator knob and repeat standardization procedure until both pH 7 and pH 4 buffers agree.

Weigh 5 g of soil into a 28 g (1 oz) paper cup or a 50 mL beaker.

Add 5 mL of deionized water.

Mix thoroughly for 5 sec with a glass or plastic stirring rod.

Let stand for 10 min.

Insert electrodes into suspension, swirling slightly.

Read pH immediately and report as pH (1:1 soil:water).

7.0 Safety

Read Material Safety Data Sheets

Wear gloves when handling standard and chemicals

Wear safety glasses while performing this procedure.

8.0 Notes

None

9.0 Attachments

None

APPENDIX B-2

LAB PROCEDURES FOR ORGANIC CARBON: ASA METHOD 29-3.5

Determination of Organic Carbon Content in Soils
ASA 29-3.5

1.0 Purpose

This procedure provides a method for determination of the proportion of organic carbon in soil using a digestion and titration method.

2.0 Scope

Soil samples containing less than 8 mg carbon can be digested and titrated.

3.0 Summary

A sample of soil containing less than 8 mg carbon (typically 100 to 500 mg) is placed into a Folin-Wu tube and digested for at 150 °C for 30 minutes with 5mL 1.00 N $K_2Cr_2O_7$ and 7.5 mL H_2SO_4. Contents of the tube are transferred to an Erlenmeyer flask and titrated with 0.2 N ferrous ammonium sulfate using N-phenylanthranillic acid as an indicator.

4.0 References

Nelson, D.W. and L.E. Sommers. 1975. A rapid and accurate procedure for estimation of organic carbon in soils. Indiana Acad. Sci. Proc. 84:456-462.

5.0 Requirements

5.1 Prerequisites

Material Safety Data Sheets (MSDS) are available for $K_2Cr_2O_7$, H_2SO_4, ferrous ammonium sulfate, and N-phenylanthranillic acid.

Soil should be air-dried and ground to less than 100 mesh.

Folin-Wu tubes and Erlenmeyer flasks should be washed with detergent, rinsed with water, nitric acid, methanol, and a final thorough rinse with water. All glassware should be completely dried before use.

Potassium dichromate (50 g or greater) should be dried at 140 °C.

5.2 Apparatus/Equipment

Folin-Wu tubes

125 mL Erlenmeyer flasks

Variable speed magnetic stirrer with illuminated top.

Teflon-coated stirring bars

Analytical balance capable of weighing to 0.1 mg

50 mL buret

Aluminum block digestor capable of heating at 150 °C

Pipettes for delivering standards and reagents

5.3 Reagents and Standards

5.3.1 Reagents

Concentrated H_2SO_4

Indicator solution—Dissolve 0.1 g of N-phenylanthranillic acid and 0.1 g of Na_2CO_3 in 100 mL water.

5.3.2 Standards

Potassium Dichromate Solution, 1.00 N – Dissolve 49.024 g $K_2Cr_2O_7$ (dried at 140 °C) in 800 mL of HPLC grade water and dilute to 1 liter. This is the primary standard for this procedure.

Ferrous Ammonium Sulfate, 0.20 N – Dissolve 78.390 g of $Fe(NH_4)_2(SO_4)_2 \bullet 6H_20$ in 50 mL of concentrated H_2SO_4 and dilute to 1 liter with HPLC grade water.

6.0 Procedure

Weigh an amount of soil containing not greater than 8 mg carbon (usually 100 to 500 mg) into a clean, dry Folin-Wu tube.

Add 5 mL of 1.00 N $K_2Cr_2O_7$ solution and 7.5 mL of concentrated H_2SO_4 to each tube containing soil (samples) and to a set of tubes without soil (heated blank).

Add 5 mL of 1.00 N $K_2Cr_2O_7$ solution and 7.5 mL of concentrated H_2SO_4 to a set of tubes without soil that will not be heated (unheated blank).

Place digestion tube in an aluminum block preheated to 150 °C and heat at 150 ± 5 °C for exactly 30 minutes.

Remove tubes from digestion block and allow to cool for 30 minutes at room temperature.

Quantitatively transfer the contents of the tube to a 125 mL Erlenmeyer flask, and dilute to approximately 60 mL with water and add 0.3 mL of N-phenylanthranillic acid solution as the indicator.

Titrate the samples with ferrous ammonium sulfate solution until an end point color change from violet to bright green is achieved.

The unheated blank is used to standardize the ferrous ammonium sulfate. The difference between the heated and unheated blanks is used to correct for the amount of dichromate consumed by spontaneous decomposition during heating.

Compute the organic carbon content of the soil using the following equation:

$$\%OrganicC = \frac{(A)(N)(0.003)(100)}{Wt}$$

$$A = \left[\left(\frac{UB - HB}{UB}\right)(HB - S)\right] + (HB - S)$$

Where **N** is the normality of the ferrous ammonium sulfate solution, **UB** is the titration value from the unheated blank, **HB** is the titration value from the heated blank, **Wt** is the weight of the sample in grams, and **S** is the titration value from the sample.

7.0 Safety

Read Material Safety Data Sheets

Wear gloves when handling standard and chemicals

Wear safety glasses while performing this procedure.

8.0 Notes

None

9.0 Attachments

None

APPENDIX B-3

LAB PROCEDURES FOR SOIL PARTICLE SIZE: ASA METHOD 15-5

Determination of Soil Particle by the Hydrometer Method ASA 15-5

1.0 Purpose

This procedure provides a method for determining the sand, silt, and clay particle size contents in soil using the hydrometer method.

2.0 Scope

Soil particle size analysis using the hydrometer method is a nondestructive method that provides for multiple measurements on the same suspension.

3.0 Summary

A 40.0 g sample of soil is mixed with 250 mL deionized water and 100 mL HMP in a 600 mL beaker and allowed to soak overnight. Samples are transferred to an electric blender, mixed for 5 min, and transferred to a sedimentation cylinder. Samples are brought up to 1.0 L and hydrometer measurements taken after 30 sec, 60 sec, 1.5 hr, and 24 hr. Results are given as percentages of sand, silt, and clay in the soil.

4.0 References

G.W. Gee and J.W. Bauder. 1986. Particle-size Analysis. Pages 383-411 in (A. Klute, ed.) Methods of Soil Analysis, Part I. Physical and Mineralogical Methods. Agronomy Monograph no. 9 (2nd Edition).

5.0 Requirements

5.1 Prerequisites

Material Safety Data Sheets (MSDS) are available for sodium hexametaphosphate and amyl alchohol

5.2 Apparatus/Equipment

Electric blender

Standard hydrometer, ASTM no. 152 H, with Bouyoucos scale in g/L

Plugger or rubber stopper for 1000 mL sedimentation cylinder

600 mL beakers

Sedimentation cylinders with a 1-L mark 36 ± 2 cm from the bottom of the inside

Electric drying oven

Drying tins

5.3 Reagents and Standards

Sodium hexametaphosphate (HMP) solution (50 g/L)

Amyl alcohol

6.0 Procedure

Weigh 10 g of soil into a drying tin for determination of oven dry weight. Dry for 24 hr at 105 °C, cool, and weigh.

Weigh 40.0 g of soil into a 600 mL beaker, add 250 mL of distilled water and 100 mL of HMP solution, and allow sample to soak overnight. Sample size may vary from 10-20 g for fine-textured soils such as silts and clays to 60-100 g for coarse-textured sands.

Transfer sample to an electric blender and blend for 5 min. Transfer to a sedimentation cylinder and add distilled water to bring the volume to 1 L.

Add 100 mL HMP solution to an addition sedimentation cylinder and add water to 1.0 L. This will be hydrometer blank.

Allow suspensions and blank to equilibrate thermally and record temperature.

Mix contents by inserting a plunger into the cylinder or by sealing the cylinder with a rubber stopper and shaking end-over-end for 1 minute. Add one drop of amyl alcohol if foaming occurs.

As soon as mixing is completed, take hydrometer reading at 30 sec, 60 sec, 1.5 hr, and 24 hr for the samples and the blank. Remove hydrometer, rinse, and wipe it dry between samples and readings. Take a temperature reading for each sample and blank when hydrometer readings are taken.

Determine the effective particle diameter X_t for each time t (30 sec, 60 sec, 1.5hr, and 24hr)

$$X = \theta t^{-1/2}$$

where θ is the sedimentation parameter.

Determine the summation percentage P_t for each time t.

$$P = \left(\frac{R - R_L}{C_0} \right) 100$$

where R is the hydrometer reading for the sample in g/L, R_L is the hydrometer reading of the blank, and C_0 is the oven-dry weight of the soil sample.

Compute the clay fraction, P_{clay}, from:

$$P_{clay} = \left[\frac{P_{1.5} - P_{24}}{\ln\left(\frac{X_{1.5}}{X_{24}} \right)} \right] \ln\left(\frac{2}{X_{24}} \right) + P_{24}$$

Compute the sand fraction, P_{sand}, from:

$$P_{sand} = \left[\frac{P_{30} - P_{60}}{\ln\left(\frac{X_{30}}{X_{60}}\right)} \right] \ln\left(\frac{2}{X_{60}}\right) + P_{60}$$

Determine the percent silt by difference as:

% silt = 100 - (% sand + % clay)

7.0 Safety

Read Material Safety Data Sheets

Wear gloves while handling chemicals.

Wear safety glasses during this procedure

8.0 Notes

None

9.0 Attachments

None

APPENDIX B-4

LAB PROCEDURES FOR TEAR GAS COMPONENTS BY GC:

METHOD AP-0046

1.0 PURPOSE

This procedure provides a method for determination of the concentrations of chloroform, chloropicrin, and chloroacetophenone by using gas chromatography and a electron capture detector for the final measurement. These three compounds are the components of tear gas (CNS).

2.0 SCOPE

This procedure applies to the measurement of chloroform, chloropicrin and chloroacetophenone in soils at levels greater than ten ppb.

3.0 SUMMARY

The analytes are extracted with HPLC grade hexane. The resulting extracted solution is then injected into a megabore capillary gas chromatography column. The three analytes are separated as they pass through the column. Their presence in the effluent is determined by a electron capture detector (ECD) and quantified by comparison to chromatograms obtained from known standards.

4.0 REFERENCES

4.1 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, Third Edition, Most Recent Update (September 1994)

Chapter 1, "Quality Assurance"

Chapter 4, "Organic Analysis"

EPA Method 8000A, "Gas Chromatography"

4.2 Manna, L.E., Toxicological and Environmental Chemistry, " A GC Method to Determine o-chloroacetophenone Residual in Soil and Vegetable Substrates",vol. 15, pp 207-215 (1987)

4.3 Gerbino. T.C., Journal of Chromatography, " Extraction and Gas Chromatographic Determination of Chlorinated Solvents in Contaminated Soil", vol.623, pp 123-127 (1987)

5.0 RESPONSIBILITIES

5.1 The Analytical Laboratory Manager, or his designee, shall ensure that this procedure is followed during the extraction and determination of tear gas from soil.

5.2 The Laboratory Supervisor, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure and is responsible for the training of new personnel for this procedure. The Laboratory Supervisor shall inspect the results of this procedure.

5.3 The analyst shall follow this procedure and report any abnormal results to the Laboratory Supervisor.

6.0 REQUIREMENTS

6.1 Prerequisites

None

6.2 Limitations and Actions

6.2.1 Delayed extractions can result in the loss of some of the components of interest. Percent recovery must be shown by use of spikes.

6.2.2 Samples shall be refrigerated upon receipt and analyzed as soon as possible.

6.3. Apparatus/Equipment

6.3.1 Analytical balance: Capacity of at least 160 g and capable of weighing to 0.1 mg.

6.3.2 Varian 3600 Gas Chromatograph equipped with a electron capture detector and integrator or computer to determine peak areas.

6.3.3 DB-5MS column: 30m x 0.53 mm inside diameter (ID).

6.3.4 GC autosampler capable of injecting one microliter of sample and performing syringe flush between sample injections.

6.3.5 Parafilm - laboratory grade film

6.3.6 Nitrogen gas - ultra high purity (99.999%)

6.3.7 Helium gas - ultra high purity (99.999%)

6.3.8 Reciprocating shaker

6.4 Reagents and Standards

6.4.1 Reagents

6.4.1.1 Hexane: HPLC grade.

6.4.1.2 Chloroform - purity of 99% or greater.

6.4.1.3 Chloropicrin - purity of 99% or greater.

6.4.1.4 Chloroacetophenone - purity of 99% or greater.

6.4.2 Standards

6.4.2.1 Stock CNS Standards

Note: After preparing the following standards in volumetric flasks, stopper them and cover with Parafilm. Standards are stored at 4° C.

6.4.2.1.1 500 ppm mixed CNS stock standard: Dissolve approximately 0.05 g, (weighed to the nearest 0.1 mg), each of chloroform, chloropicrin, and chloroacetophenone in hexane. Dilute to 100 ml with hexane.

6.4.2.1.2 1 ppm (1000 ppb) mixed CNS standard: Dilute 1.0 ml of the 500 ppm CNS stock standard to 500 ml with hexane.

6.5 Quality Control Sample Requirements

6.5.1 The following quality control (QC) samples shall be included with each batch of samples processed by this procedure.

a. Duplicate sample
b. Matrix spike
c. Method blank
e. Laboratory Control Sample (LCS)

6.5.2 A midpoint calibration check and reagent blank shall be run at the start of every run, every ten injections, and at the end of the run.

7.0 **PROCEDURE**

7.1 Calibration

7.1.1 At the beginning of each batch, prepare at least five concentration levels of the calibration standards by adding accurately measured volumes of stock 1 ppm standard to a volumetric flask and diluting to volume with hexane. One of the standards should be at a concentration near the method detection limit (MDL), and the other concentrations should correspond to the expected linear range of the device and should cover the range of concentrations found in real samples (see 7.1.2). Use volumetric pipettes for all additions.

7.1.2 Calibration standards in the range of 10, 50, 100, 250, and 500 ppb respectively, may be prepared as follows into 100 ml volumetric flasks:

Calibration standard ppb	Standard solution ppm	Aliquot ml
10	1	1
50	1	5.0
100	1	10
250	1	25
500	1	50

7.1.3 For each run, utilize Fison Multichrom vendor-supplied chromatography workstation software to calculate a separate calibration curve for chloroform, chloropicrin, and chloroacetophenone will be calculated using the standards from 7.1.2.

7.2 Procedure Instructions

7.2.1 Extraction of Soil Samples

7.2.1.1 Remove the cap, pipette 50 ml of hexane into the sample container and immediately return the cap.

7.2.1.2 Prepare a matrix spike sample, when possible, by adding 50 ml hexane and 1 ml of 500 ppm mixed standard to a duplicate soil sample as in Step 7.2.1.1.

7.2.1.3 Shake the samples on a reciprocating shaker for approximately 2 hours. Allow to settle. Based on known experimental conditions, dilute an aliquot of the sample with hexane using volumetric glassware to bring it into the calibration range.

7.2.1.4 Pipette 1 ml of the diluted sample into an autosampler vial. If the sample is cloudy, filter through a syringe filter into the autosampler vial. Proceed from 7.2.3.

7.2.2 Previously Prepared Hexane Extracts

7.2.2.1 Prepare a matrix spike sample, when possible, by adding 1 ml 500 ppm mixed standard to a duplicate extract sample or portion of an extract sample. (Other concentration of standard may be used where needed to remain in the calibration range.)

7.2.2.2 Based on known experimental conditions, dilute an aliquot of each sample with hexane using volumetric glassware to bring it into the calibration range.

7.2.2.3 Pipette 1 ml of the diluted sample into an autosampler vial. If the hexane layer is cloudy, filter through a syringe filter into the autosampler vial.

7.2.3 Load the sample into the autosampler and submit for analysis with the following parameters:

a. Column: DB-5MS
b. Injector: 200° C
c. Detector: 350° C
d. Temperatures: Column oven: 40° C for 10 min., ramp to 150° C at rate of 15°C/min. and hold for 13` min.
e. Make-up gas: Nitrogen 26 ml/min
f. Carrier gas: Helium 8.2 ml/min
g. Injection volume: 1 microliter
h. Run time: 30.33 min.

7.3 Calculations and Recording Data

7.3.1 Determine the concentration of the individual compounds in the sample from their area responses using the calibration curve. Use Fison Multichrom software.

7.3.2 Calculate the percent recovery of the spiked samples.

$$\% \text{ Recovery} = \frac{\text{Obtained Response (ppm)}}{\text{Known concentration (ppm)}} * 100$$

7.3.3 Collect all chromatograms. Record all data on worksheets. Attach all of these records to the request sheets for filing.

8.0 **SAFETY**

8.1 Read Material Safety Data Sheets.

8.2 Wear gloves when handling standards and chemicals.

8.3 Wear safety glasses when performing this procedure.

8.4 Operations with samples known to contain tear gas components or concentrated solutions of components should be carried out in a hood.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

APPENDIX B-5

LAB PROCEDURES FOR DETERMINATION OF ^{14}C RADIOACTIVITY BY SCINTILLATION COUNTING

Determination of ^{14}C Radioactivity by Liquid Scintillation Counting Packard 1900TR

1.0 PURPOSE

This procedure provides a method for optimizing liquid scintillation counting parameters and for determining radioactivity in terms of disintegrations of Carbon-14 (^{14}C) per minute using liquid scintillation counting.

2.0 SCOPE

This procedure applies to liquid samples in aqueous and organic solutions containing ^{14}C.

3.0 SUMMARY

An aqueous or organic solution of chemicals containing ^{14}C is added to a glass scintillation vial. Liquid scintillation cocktail is added in proportions to give a clear liquid or a translucent gel, without phase separation. The presence of ^{14}C -chemicals in the scintillation cocktail is determined by the counts per minute produced in an energy-discriminated window. The amount of radioactivity is quantified by comparison to a set of blanks and standards. Results are corrected for quenching by comparison to a set of quench standards.

4.0 REFERENCES

4.1 Packard Instrument Company. 1990. Tri-Carb Liquid Scintillation Analyzers Model 1900TR: Operation Manual. Publication No. 169-4066 Rev. A.

4.2 Nuclear Regulatory Commission License No. 41-25370-01.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the research supervisor to assess data and review operational conditions. The research supervisory shall delegate performance of this procedure to technicians who are trained in handling radioactive material.

5.2 It is the responsibility of the technician to adhere to this procedure, to log data, and to report unusual conditions to the supervisor.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Radioactive material must be handled, stored and disposed in accordance with the requirements of Resource Group's Radioactive Materials License.

6.1.2 Laboratory personnel shall have had training on radiation safety and safe handling of radioactive materials.

6.2 Limitations and Actions

6.2.1 Calibration solutions should be made to match the concentration of major sample components as far as feasible.

6.2.2 Labeling on scintillation vials should be restricted to the caps and should not cover the sides of the vial.

6.3 Apparatus/Equipment

6.3.1 Packard Scintillation Counter capable of detecting ^{14}C

6.3.2 Scintillation vials - glass - 20 ml volume.

6.3.2 Scintillation vial caps - aluminum lined and plastic lined.

6.4 Reagents and Standards

6.4.1 Liquid scintillation cocktail appropriate to the solvent in the samples being studied - Example: Packard Ultima Gold is a biodegradable scintillation cocktail designed for aqueous solutions which tolerates sodium hydroxide fairly well.

6.4.2 Automatic dispensing pipettors for dispensing scintillation cocktail

6.4.3 Liquid scintillation quench standards - Packard part no. 6018595.

6.4.4 ^{14}C standards - Solutions of ^{14}C -labeled chloroform, chloropicrin, and 2-chloroacetophenone with known disintegration rates and concentrations of chloroform, chloropicrin, or 2-chloroacetophenone.

6.5 Quality Control Sample Requirements

6.5.1 Examine quench curve parameters after each run. Quench curves remain fairly constant for weeks. Any abrupt changes indicate the need for maintenance.

6.5.2 Examine and record counting efficiency for each sample type, scintillation cocktail, and sample-to-cocktail ratio.

7.0 <u>PROCEDURE</u>

7.1 Choosing a Scintillation Cocktail

Utilizing manufacturer's information, choose a scintillation cocktail which will dissolve the major constituent in the samples of interest. Whenever possible, use a biodegradable cocktail. When a biodegradeable cocktail is not available for the samples of interest, choose a cocktail without flammable constituents if that is possible.

7.2 Mixing Calibration Standards and Blanks

7.2.1 Assess sample constituents and concentrations for use in the next step. We wish to match the solubility characteristics of the samples and standards in the scintillation cocktail as much as possible.

7.2.1 Measure an amount of ^{14}C standard into a volumetric flask to produce a final disintegration rates of no less than 2000 counts per minute..

7.2.2 Add major solution constituents such as sodium hydroxide or organic solvents to match sample concentrations.

7.2.3 Bring the flask to volume with the same solvent as the samples.

7.2.4 For the blank, omit the ^{14}C standard, but add major solutions constituents and solvent as listed above.

7.3 Selecting a Ratio of Cocktail to Sample

7.3.1 Utilizing a calibration standard made to match the concentration of major constituents in the samples to be measured, produce a series of mixtures of cocktail and standard solution in various ratios (10:1, 10:2, 10:3 etc.).

7.3.2 Shake the samples well. Examine them after a few minutes to ensure they have not separated into two phases and submit them for counting.

7.3.3 After counting, examine the samples. Either a clear solution or translucent gel should be produced with no layering at twenty-four hours. Utilize the ratio with the highest count rate. Reject any samples which show two layers or a precipitate.

7.3.4 Log all ratios, count results, sample descriptions in a research notebook.

7.4 Scintillation Counter Protocol

7.4.1 Access the protocol editing screen, select a protocol number and apply the following choices.

Count time:	(See 7.5 below)
2 Sigma Coincidence:	yes
Radionuclide:	14C
2 Sigma 5:	A=0.5
	B=0.0
	C=0.0
QIP:	tSIE/AEC
# Counts/vial:	1
# Vials/std:	1
1st vial background:	yes
Data Mode:	DPM
DPM Standards Data:	Count
Constant Quench:	no
# Stds/nuclide:	10
Nuclide 1:	DPM from label on quench standards

7.4.2 Save the settings and note the protocol number.

7.5 Selecting a Count Time

7.5.2 If a count rate for a sample set cannot be estimated, perform a preliminary count of four minutes for all samples.

7.5.1 Using an estimate of the count rate or the result of a four minute count, select a count time from four to sixty minutes.

7.5.1.1 Count times should be selected so that the standard gives totals counts (count rate * count time) no less than 10,000.

7.5.1.2 The count time should be selected so that the lowest sample gives a net count of 400 counts ([sample rate - background rate]*count time) above background, whenever possible.

7.5.1.3 In cases of extremely low count rates in samples, utilize counts up to sixty minutes duration.

7.6 Loading and Counting Samples

7.6.1 Select a vial cassette and the protocol plug which matches the protocol number being used.

7.6.2 Mix samples, a vial background blank, and a standard with the correct cocktail as recorded in the research logbook. Use the correct ratio of cocktail to sample as recorded in the research logbook.

7.6.3 Cap the samples. Use aluminum-lined caps for all but basic solutions. Shake well.

7.6.4 Load samples and standards in the following order: Vial background sample, quench samples in numerical order, ^{14}C standards, then samples.

7.6.5 Load cassettes onto sample changer. Slide the protocol plug flag to the "out" position.

7.6.6 Exit the Protocol editor and start sample counting.

7.7 After counting, examine the data printouts and scintillation vials.

7.7.1 If any vials have separated into two layers, note that on the printouts and resubmit the samples for another count after shaking well. In this case, omit the quench standards so that counting may be accomplished before phase separation. Use values from the previously determined quench curve for quench correction.

7.7.2 Examine quench curve parameters after each run. Quench curves remain fairly constant for weeks. Any abrupt changes indicate the need for maintenance.

7.7.3 Log the counting efficiency in a research notebook or machine log.

8.0 Safety

8.1 Read Material Safety Data Sheets

8.2 Wear gloves, safety glasses, and lab coats during this procedure

8.3 Keep a Geiger counter in the vicinity to alert you in case of accidental spillage.

8.4 Protect work surfaces from accidental spillage of radioactive materials by using disposal, plastic- backed countertop covers.

8.5 Be alert to accidental spread of radioactive materials that may be carried on gloves or laboratory apparatus.

8.6 In case of a spill, contact Jesse Coleman (386-2993) for Health Physics support.

9.0 NOTES

None

10.0 ATTACHMENTS

None

END OF PROCEDURE

APPENDIX B-6

LAB PROCEDURES FOR SOIL PARTICLE SIZE: ASTM METHOD D422

Designation: D 422 – 63 (Reapproved 1990)ε1

Standard Test Method for Particle-Size Analysis of Soils[1]

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε1 NOTE—Section 19 was added editorially in September 1990.

1. Scope

1.1 This test method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-μm), or No. 200 (75-μm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (*1*) a high-speed mechanical stirrer, and (*2*) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-μm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μm.

2. Referenced Documents

2.1 *ASTM Standards:*

D 421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft³/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

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[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

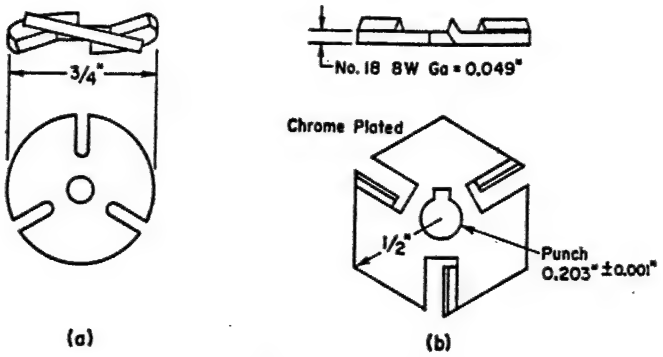
Current edition approved Nov. 21, 1963. Originally published 1935. Replaces D 422 – 62.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.



Metric Equivalents					
in.	0.001	0.049	0.203	½	¾
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles

3-in. (75-mm)	No. 10 (2.00-mm)
2-in. (50-mm)	No. 20 (850-μm)
1½-in. (37.5-mm)	No. 40 (425-μm)
1-in. (25.0-mm)	No. 60 (250-μm)
¾-in. (19.0-mm)	No. 140 (106-μm)
⅜-in. (9.5-mm)	No. 200 (75-μm)
No. 4 (4.75-mm)	

NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)	No. 16 (1.18-mm)
1½-in. (37.5-mm)	No. 30 (600-μm)
¾-in. (19.0-mm)	No. 50 (300-μm)
⅜-in. (9.5-mm)	No. 100 (150-μm)
No. 4 (4.75-mm)	No. 200 (75-μm)
No. 8 (2.36-mm)	

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-mL capacity.

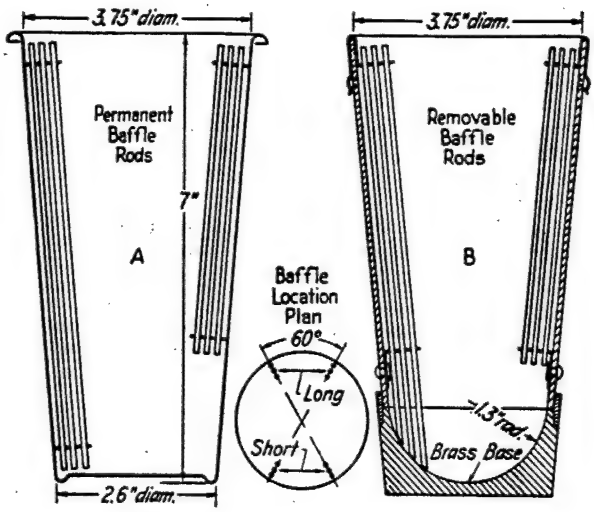
3.9 *Timing Device*—A watch or clock with a second hand.

4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall



Metric Equivalents			
in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

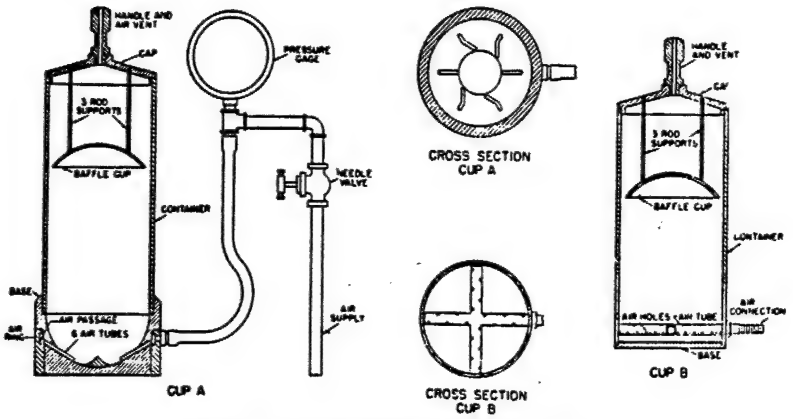


FIG. 3 Air-Jet Dispersion Cups of Apparatus B

5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Practice D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Practice D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
⅜ (9.5)	500
¾ (19.0)	1000
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

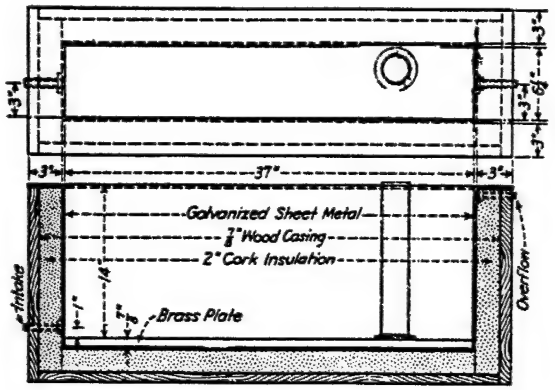
5.2 Provision is made in Section 5 of Practice D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.



Metric Equivalents						
in.	⅞	1	3	6¼	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-mm) SIEVE

7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cyclinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hydrometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2. washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

9.5 Place the cover cap on the cup and open the air control valve until the gage pressure is 20 psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil - water slurry to the sedimentation cylinder.

10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns.

Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-μm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

CALCULATIONS AND REPORT

12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

14. Percentages of Soil in Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.

TABLE 1 Values of Correction Factor, a, for Different Specific Gravities of Soil Particles[A]

Specific Gravity	Correction Factor[A]
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100$$

where:

a = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),
P = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,
R = hydrometer reading with composite correction applied (Section 7),
W = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,
G = specific gravity of the soil particles, and
G_1 = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G_1.

15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. According to Stokes' law:

$$D = \sqrt{[30n/980(G - G_1)]} \times L/T$$

where:

D = diameter of particle, mm,

n = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

L = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

T = interval of time from beginning of sedimentation to the taking of the reading, min,

G = specific gravity of soil particles, and

G_1 = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows:

$$D = K\sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

15.3 Values of D may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of L is divided by T using the A- and B-scales, the square root being indicated on the D-scale. Without ascertaining the value of the square root it may be multiplied by K, using either the C- or CI-scale.

16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2), and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.6
1.005	15.0	5	15.5		
1.006	14.7	6	15.3	36	10.4
1.007	14.4	7	15.2	37	10.2
1.008	14.2	8	15.0	38	10.1
1.009	13.9	9	14.8	39	9.9
1.010	13.7	10	14.7	40	9.7
1.011	13.4	11	14.5	41	9.6
1.012	13.1	12	14.3	42	9.4
1.013	12.9	13	14.2	43	9.2
1.014	12.6	14	14.0	44	9.1
1.015	12.3	15	13.8	45	8.9
1.016	12.1	16	13.7	46	8.8
1.017	11.8	17	13.5	47	8.6
1.018	11.5	18	13.3	48	8.4
1.019	11.3	19	13.2	49	8.3
1.020	11.0	20	13.0	50	8.1
1.021	10.7	21	12.9	51	7.9
1.022	10.5	22	12.7	52	7.8
1.023	10.2	23	12.5	53	7.6
1.024	10.0	24	12.4	54	7.4
1.025	9.7	25	12.2	55	7.3
1.026	9.4	26	12.0	56	7.1
1.027	9.2	27	11.9	57	7.0
1.028	8.9	28	11.7	58	6.8
1.029	8.6	29	11.5	59	6.6
1.030	8.4	30	11.4	60	6.5
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

[A] Values of effective depth are calculated from the equation:

$$L = L_1 + \tfrac{1}{2}\,[L_2 - (V_B/A)]$$

where:

L = effective depth, cm,

L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,

L_2 = overall length of the hydrometer bulb, cm,

V_B = volume of hydrometer bulb, cm^3, and

A = cross-sectional area of sedimentation cylinder, cm^2

Values used in calculating the values in Table 2 are as follows:

For both hydrometers, 151H and 152H:

L_2 = 14.0 cm

V_B = 67.0 cm^3

A = 27.8 cm^2

For hydrometer 151H:

L_1 = 10.5 cm for a reading of 1.000

= 2.3 cm for a reading of 1.031

For hydrometer 152H:

L_1 = 10.5 cm for a reading of 0 g/litre

= 2.3 cm for a reading of 50 g/litre

TABLE 3 Values of K for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

Temperature, °C	Specific Gravity of Soil Particles								
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149

arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.

NOTE 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(*1*) Gravel, passing 3-in. and retained on No. 4 sieve ..... %
(*2*) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %
  (*a*) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %
  (*b*) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %
  (*c*) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %
(*3*) Silt size, 0.074 to 0.005 mm ..... %
(*4*) Clay size, smaller than 0.005 mm ..... %
  Colloids, smaller than 0.001 mm ..... %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS

Sieve Size	Percentage Passing
3-in.	.....
2-in.	.....
1½-in.	.....
1-in.	.....
¾-in.	.....
⅜-in.	.....
No. 4 (4.75-mm)	.....
No. 10 (2.00-mm)	.....
No. 40 (425-μm)	.....
No. 200 (75-μm)	.....

HYDROMETER ANALYSIS

0.074 mm	.....
0.005 mm	.....
0.001 mm	.....

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

19. Keywords

19.1 grain-size; hydrometer analysis; hygroscopic moisture; particle-size; sieve analysis

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APPENDIX B-7

LAB PROCEDURES FOR KINEMATIC VISCOSITY: ASTM METHOD D 445-94

Designation: D 445 – 94ε1

An American National Standard
British Standard 2000: Part 71:1990

Designation: 71/95

Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)[1]

This standard is issued under the fixed designation D 445; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This test method has been approved by the sponsoring committee and accepted by the Cooperating Societies in accordance with established procedures.

This standard has been approved for use by agencies of the Department of Defense and replaces Method 305.6 of Federal Test Method Standard 791b. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

ε1 NOTE—Section 3 was corrected editorially in July 1995.

1. Scope

1.1 This test method specifies a procedure for the determination of the kinematic viscosity, ν, of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η, can be obtained by multiplying the measured kinematic viscosity by the density, ρ, of the liquid.

NOTE 1—For the measurement of the kinematic viscosity and viscosity of bitumens, see also Test Methods D 2170 and D 2171.

1.2 The result obtained from this test method is dependent upon the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional (Newtonian flow behavior). If, however, the viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameters. The procedure and precision values for residual fuel oils, which under some conditions exhibit non-Newtonian behavior, have been included.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers[2]

D 1193 Specification for Reagent Water[3]

D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer[2]

D 1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer[2]

D 2170 Test Method for Kinematic Viscosity of Asphalts (Bitumens)[4]

D 2171 Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer[4]

E 1 Specification for ASTM Thermometers[5]

E 77 Test Method for the Inspection and Verification of Thermometers[5]

2.2 *ISO Standards:*[6]

ISO Guide 25—General Requirements for the Calibration and Testing Laboratories

ISO 3104 Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity

ISO 3105 Glass Capillary Kinematic Viscometers—Specification and Operating Instructions

ISO 3696 Water for Analytical Laboratory Use—Specification and Test Methods

ISO 9000 Quality Management and Quality Assurance Standards—Guidelines for Selection and Use

3. Terminology

3.1 *Description of Terms Specific to This Standard:*

3.1.1 *density, n*—the mass per unit volume of a substance at a given temperature.

3.1.2 *dynamic viscosity, n*—the ratio between the applied shear stress and rate of shear of a liquid.

DISCUSSION 1—It is sometimes called the coefficient of dynamic viscosity or, simply, viscosity. Thus dynamic viscosity is a measure of the resistance to flow or deformation of a liquid.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

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In the IP, this test method is under the jurisdiction of the Standardization Committee

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 04.03.

[5] *Annual Book of ASTM Standards*, Vol 14.03.

[6] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

DISCUSSION—The term dynamic viscosity can also be used in a different context to denote a frequency-dependent quantity in which shear stress and shear rate have a sinusodial time dependence.

3.1.3 *kinematic viscosity, n*—the resistance to flow of a fluid under gravity.

DISCUSSION—For gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, ρ. For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, ν, where $\nu = \eta/\rho$, and η is the dynamic viscosity coefficient.

4. Summary of Test Method

4.1 The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer.

5. Significance and Use

5.1 Many petroleum products, and some non-petroleum materials, are used as lubricants, and the correct operation of the equipment depends upon the appropriate viscosity of the liquid being used. In addition, the viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate measurement of viscosity is essential to many product specifications.

6. Apparatus

6.1 *Viscometers*—Use only calibrated viscometers of the glass capillary type, capable of measuring kinematic viscosity within the limits of precision given in Section 15.

6.1.1 Viscometers listed in Table A1.1, whose specifications meet those given in Specification D 446 and in ISO 3105 meet these requirements. It is not intended to restrict this test method to the use of only those viscometers listed in Table A1.1. Annex A1 gives further guidance.

6.1.2 *Automation*—Automated viscometers, which have been shown to measure kinematic viscosity within the limits of precision given in Section 15 are acceptable alternatives. Apply a kinetic energy correction (see Specification D 446 and ISO 3105) to kinematic viscosities less than 10 mm^2/s and flow times less than 200 s.

6.2 *Viscometer Holders*—Use viscometer holders to enable all viscometers which have the upper meniscus directly above the lower meniscus to be suspended vertically within 1° in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within 0.3° in all directions (see Specification D 446 and ISO 3105).

6.2.1 The proper alignment of vertical parts may be confirmed by using a plumb line, but for rectangular baths with opaque ends this may not be wholly satisfactory.

6.3 *Temperature-Controlled Bath*—Use a transparent liquid bath of sufficient depth such that at no time during the measurement any portion of the sample in the viscometer is less than 20 mm below the surface of the bath liquid or less than 20 mm above the bottom of the bath.

6.3.1 *Temperature Control*—For each series of flow time measurements, the temperature control of the bath liquid shall be such that within the range from 15 to 100°C, the temperature of the bath medium does not vary by more than ±0.02°C of the selected temperature over the length of the viscometer, or between the position of each viscometer, or at

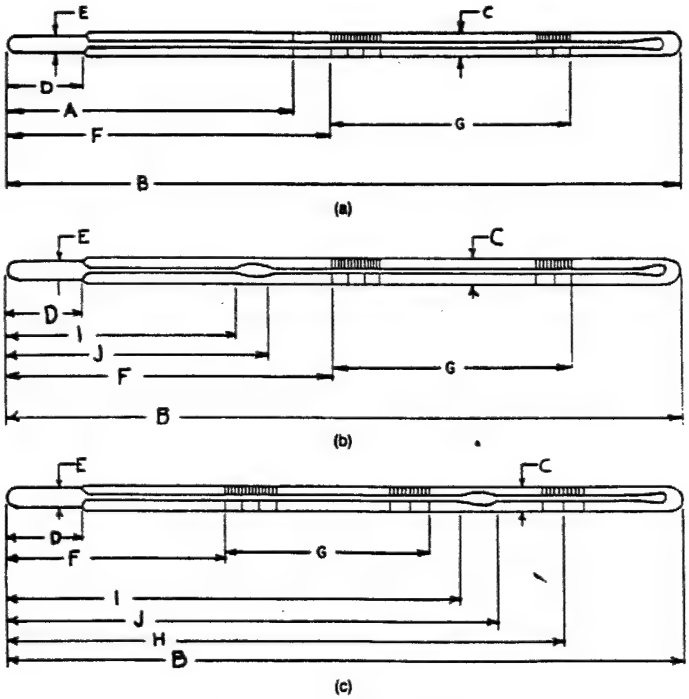

FIG. 1 Thermometer Designs

the location of the thermometer. For temperatures outside this range, the deviation from the desired temperature must not exceed ±0.05°C.

6.4 *Temperature Measuring Device in the Range from 0 to 100°C*—Use either calibrated liquid-in-glass thermometers (Annex A2) of an accuracy after correction of ±0.02°C or better, or any other thermometric device of equal or better accuracy.

6.4.1 If calibrated liquid-in-glass thermometers are used, the use of two thermometers is recommended. The two thermometers shall agree within 0.04°C.

6.4.2 Outside the range from 0 to 100°C, calibrated liquid-in-glass thermometers of an accuracy after correction of ±0.05°C or better shall be used, and when two thermometers are used in the same bath they shall agree within ±0.1°C.

6.5 *Timing Device*—Use any timing device that is capable of taking readings with a discrimination of 0.1 s or better, and has an accuracy within ±0.07 % (see Annex A3) of the reading when tested over intervals of 200 and 900 s.

6.5.1 Electrical timing devices may be used if the current frequency is controlled to an accuracy of 0.05 % or better. Alternating currents, as provided by some public power systems, are intermittently rather than continuously controlled. When used to actuate electrical timing devices, such control can cause large errors in viscosity flow measurements.

7. Reagents and Materials

7.1 *Chromic Acid Cleaning Solution*, or a nonchromium-containing, strongly oxidizing acid cleaning solution.

NOTE 2: **Warning**—Chromic acid is a health hazard. It is toxic, a recognized carcinogen, highly corrosive, and potentially hazardous in contact with organic materials. If used, wear a full face-shield and full-length protective clothing including suitable gloves. Avoid breathing vapor. Dispose of used chromic acid carefully as it remains hazardous. Nonchromium-containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium which has special disposal problems.

7.2 *Sample Solvent*, completely miscible with the sample. Filter before use.

7.2.1 For most samples a volatile petroleum spirit or naphtha is suitable. For residual fuels, a prewash with an aromatic solvent such as toluene or xylene may be necessary to remove asphaltenic material.

7.3 *Drying Solvent*, a volatile solvent miscible with the sample solvent (7.2) and water (7.4). Filter before use.

7.3.1 Acetone is suitable.

7.4 *Water*, deionized or distilled and conforming to Specification D 1193 or Grade 3 of ISO 3696. Filter before use.

8. Calibration and Verification

8.1 *Viscometers*—Use only calibrated viscometers, thermometers, and timers as described in Section 6.

8.2 *Certified Viscosity Reference Standards*[7] *(Table A2)*—These are for use as confirmatory checks on the procedure in the laboratory.

8.2.1 If the measured kinematic viscosity does not agree within ±0.35 % of the certified value, recheck each step in the procedure, including thermometer and viscometer calibration, to locate the source of error. Annex A1 gives details of standards available.

8.2.2 The most common sources of error are caused by particles of dust lodged in the capillary bore and temperature measurement errors. It must be appreciated that a correct result obtained on a standard oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

8.3 The calibration constant, C, is dependent upon the gravitational acceleration at the place of calibration and this must, therefore, be supplied by the standardization laboratory together with the instrument constant. Where the acceleration of gravity, g, differs by more that 0.1 %, correct the calibration constant as follows:

$$C_2 = (g_2/g_1) \times C_1 \quad (1)$$

where the subscripts 1 and 2 indicate, respectively, the standardization laboratory and the testing laboratory.

9. General Procedure for Kinematic Viscosity

9.1 Adjust and maintain the viscometer bath at the required test temperature within the limits given in 6.3.1 taking account of the conditions given in Annex A2 and of the corrections supplied on the certificates of calibration for the thermometers.

9.1.1 Thermometers shall be held in an upright position under the same conditions of immersion as when calibrated.

9.1.2 In order to obtain the most reliable temperature measurement, it is recommended that two thermometers with valid calibration certificates be used (see 6.4).

9.1.3 They should be viewed with a lens assembly giving approximately five times magnification and be arranged to eliminate parallax errors.

9.2 Select a clean, dry, calibrated viscometer having a range covering the estimated kinematic viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time shall not be less than 200 s or the longer time noted in Specification D 446.

9.2.1 The specific details of operation vary for the different types of viscometers listed in Table A1. The operating instructions for the different types of viscometers are given in Specifications D 446.

9.2.2 When the test temperature is below the dew point, affix loosely packed drying tubes to the open ends of the viscometer. The drying tubes must fit the design of the viscometer and not restrict the flow of the sample by pressures created in the instrument. Carefully flush the moist room air from the viscometer by applying vacuum to one of the drying tubes. Finally, before placing the viscometer in the bath, draw up the sample into the working capillary and timing bulb and allow to drain back as an additional safeguard against moisture condensing or freezing on the walls.

9.2.3 Viscometers used for silicone fluids, fluorocarbons, and other liquids which are difficult to remove by the use of a cleaning agent, shall be reserved for the exclusive use of those fluids except during their calibration. Subject such

[7] The ASTM Viscosity Oil Standards are available in 1-pt (0.47 L) containers. Purchase orders should be addressed to the Cannon Instrument Co., P.O. Box 16, State College, PA 16804. Shipment will be made as specified or by best means.

viscometers to calibration checks at frequent intervals. The solvent washings from these viscometers shall not be used for the cleaning of other viscometers.

10. Procedure for Transparent Liquids

10.1 Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity with that employed when the instrument was calibrated. If the sample contains solid particles, filter during charging through a (75-μm) filter (see Specifications D 446).

10.1.1 In general, the viscometers used for transparent liquids are of the type listed in Table A1.1, A and B.

10.1.2 With certain products which exhibit *gel-like* behavior, exercise care that measurements are made at sufficiently high temperatures for such materials to flow freely, so that similar kinematic viscosity results are obtained in viscometers of different capillary diameters.

10.1.3 Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Where one bath is used to accommodate several viscometers, never add or withdraw a viscometer while any other viscometer is in use for measuring a flow time.

10.1.4 Because this time will vary for different instruments, for different temperatures, and for different kinematic viscosities, establish a safe equilibrium time by trial.

10.1.4.1 Thirty minutes should be sufficient except for the highest kinematic viscosities.

10.1.5 Where the design of the viscometer requires it, adjust the volume of the sample to the mark after the sample has reached temperature equilibrium.

10.2 Use suction (if the sample contains no volatile constituents) or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark, unless any other value is stated in the operating instructions for the viscometer. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. If this flow time is less than the specified minimum (see 9.2), select a viscometer with a capillary of smaller diameter and repeat the operation.

10.2.1 Repeat the procedure described in 10.2 to make a second measurement of flow time. Record the result.

10.2.2 If the two measurements agree within the stated determinability figure (see 15.1) for the product, use the average for calculating the kinematic viscosity to be reported. If the measurements do not agree, repeat the determination after thorough cleaning and drying of the viscometer and filtering of the sample. Record the result.

11. Procedure for Opaque Liquids

11.1 For steam-refined cylinder oils and black lubricating oils, proceed to 11.3 ensuring a thoroughly representative sample is used. The kinematic viscosity of residual fuel oils and similar waxy products can be affected by the previous thermal history and the following procedure described in 11.1.1 to 11.2.2 shall be followed to minimize this.

11.1.1 In general, the viscometers used for opaque liquids are of the reverse-flow type listed in Table A1.1, C.

11.1.2 Heat in the original container, in an oven, at 60 ± 2°C for 1 h.

11.1.3 Thoroughly stir the sample with a suitable rod of sufficient length to reach the bottom of the container. Continue stirring until there is no sludge or wax adhering to the rod.

11.1.4 Recap the container tightly and shake vigorously for 1 min to complete the mixing.

11.1.4.1 With samples of a very waxy nature or oils of high kinematic viscosity, it may be necessary to increase the heating temperature above 60°C to achieve proper mixing. The sample should be sufficiently fluid for ease of stirring and shaking.

11.2 Immediately after completing 11.1.4, pour sufficient sample to fill two viscometers into a 100-mL glass flask and loosely stopper.

11.2.1 Immerse the flask in a bath of boiling water for 30 min.

NOTE 3: **Precaution**—Exercise care as vigorous boil-over can occur when opaque liquids which contain high levels of water are heated to high temperatures.

11.2.2 Remove the flask from the bath, stopper tightly, and shake for 60 s.

11.3 Charge two viscometers in the manner dictated by the design of the instrument. For example, for the cross-arm or the BS U-tube viscometers for opaque liquids, filter the sample through a 75-μm filter into two viscometers previously placed in the bath. For samples subjected to heat treatment, use a preheated filter to prevent the sample coagulating during the filtration.

11.3.1 Viscometers which are charged before being inserted into the bath may need to be preheated in an oven prior to charging the sample. This is to ensure that the sample will not be cooled below test temperature.

11.3.2 After 10 min, adjust the volume of the sample (where the design of the viscometer requires) to coincide with the filling marks as in the viscometer specifications (see Specifications D 446).

11.3.2 Allow the charged viscometers enough time to reach the test temperature (see 11.3.1). Where one bath is used to accommodate several viscometers, never add or withdraw a viscometer while any other viscometer is in use for measuring flow time.

11.4 With the sample flowing freely, measure in seconds to within 0.1 s, the time required for the advancing ring of contact to pass from the first timing mark to the second. Record the result.

11.4.1 In the case of samples requiring heat treatment described in 11.1 through 11.2.1, complete the determinations within 1 h of completing 11.2.2. Record the result.

11.5 Calculate the mean kinematic viscosity, ν, in mm^2/s, from the two determinations.

11.5.1 For residual fuel oils, if the two determinations agree within the stated determinability figure (see 15.1), use the average for calculating the kinematic viscosity to be reported. If the measurements do not agree, repeat the determination after thorough cleaning and drying of the viscometer and filtering of the sample. Record the result.

11.5.2 For other opaque liquids, no precision data is available.

12. Cleaning of Viscometer

12.1 Between successive determinations, clean the

viscometer thoroughly by several rinsings with the sample solvent, followed by the drying solvent (see 7.3). Dry the tube by passing a slow stream of filtered dry air through the viscometer for 2 min or until the last trace of solvent is removed.

12.2 Periodically clean the viscometer with the cleaning solution (**Warning**—see 7.1), for several hours to remove residual traces of organic deposits, rinse thoroughly with water (7.4) and drying solvent (7.3), and dry with filtered dry air or a vacuum line. Remove any inorganic deposits by hydrochloric acid treatment before the use of cleaning acid, particularly if the presence of barium salts is suspected.

NOTE 4: **Caution**—It is essential that alkaline cleaning solutions are not used as changes in the viscometer calibration can occur.

13. Calculation

13.1 Calculate the kinematic viscosity, ν, from the measured flow time, t, and the viscometer constant, C, by means of the following equation:

$$\nu = C \cdot t \quad (2)$$

where:

ν = kinematic viscosity, mm^2/s,
C = calibration constant of the viscometer, $(mm^2/s)/s$, and
t = mean flow time, s.

13.2 Calculate the dynamic viscosity, η, from the calculated kinematic viscosity, ν, and the density, ρ, by means of the following equation:

$$\eta = \nu \times \rho \times 10^{-3} \quad (3)$$

where:

η = dynamic viscosity, mPa·s,
ρ = density, kg/m^3, at the same temperature used for the determination of the kinematic viscosity, and
ν = kinematic viscosity, mm^2/s.

13.2.1 The density of the sample can be determined at the test temperature of the kinematic viscosity determination by an appropriate method such as Test Methods D 1217 or D 1480.

14. Expression of Results

14.1 Report the test results for the kinematic or dynamic viscosity, or both, to four significant figures, together with the test temperature.

15. Report

15.1 Report the following information:

15.1.1 Type and identification of the product tested,

15.1.2 Reference to this test method or a corresponding international standard,

15.1.3 Result of the test (see 14),

15.1.4 Any deviation, by agreement or otherwise, from the procedure specified,

15.1.5 Date of the test, and

15.1.6 Name and address of the test laboratory.

16. Precision

16.1 *Determinability (d)*—The difference between successive determinations obtained by the same operator in the same laboratory using the same apparatus for a series of operations leading to a single result, would in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C[8]	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C[9]	0.0013 y	(0.13 %)
Formulated oils at 150°C[10]	0.015 y	(1.5 %)
Petroleum wax at 100°C[11]	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C[12]	0.011 (y+8)	
Residual fuel oils at 50°C[12]	0.017 y	(1.7 %)

where: y is the average of determinations being compared.

16.2 *Repeatability (r)*—The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C[8]	0.0011 x	(0.11 %)
Formulated oils at 40 and 100°C[9]	0.0026 x	(0.26 %)
Formulated oils at 150°C[10]	0.0056 x	(0.56 %)
Petroleum wax at 100°C[11]	$0.0141\ x^{1.2}$	
Residual fuel oils at 80 and 100°C[12]	0.013 (x+8)	
Residual oils at 50°C[12]	0.015 x	(1.5 %)

where: x is the average of results being compared.

16.3 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated below only in one case in twenty.

Base oils at 40 and 100°C[8]	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C[9]	0.0076 x	(0.76 %)
Formulated oils at 150°C[10]	0.018 x	(1.8 %)
Petroleum wax at 100°C[11]	$0.0366\ x^{1.2}$	
Residual fuel oils at 80 and 100°C[12]	0.04 (x+8)	
Residual oils at 50°C[12]	0.074 x	(7.4 %)

where: x is the average of results being compared.

16.4 The precision for used oils has not been determined but is expected to be poorer than that for formulated oils. Because of the extreme variability of such used oils, it is not anticipated that the precision of used oils will be determined.

17. Keywords

17.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

[8] These precision values were obtained by statistical examination of interlaboratory results from six mineral oils in the range from 8 to 1005 mm^2/s at 40°C and from 2 to 43 mm^2/s at 100°C, and were first published in 1989. Precision data available from ASTM Headquarters. Request RR:D02-1331 and RR:D02-1132.

[9] These precision values were obtained by statistical examination of interlaboratory results from seven fully formulated engine oils in the range from 36 to 340 mm^2/s at 40°C and from 6 to 25 mm^2/s at 100°C, and were first published in 1991. Precision data available from ASTM Headquarters. Request RR:D02-1332.

[10] These precision values were obtained by statistical examination of interlaboratory results for eight fully formulated engine oils in the range from 7 to 19 mm^2/s at 150°C, and first published in 1991. Precision data available from ASTM Headquarters. Request RR:D02-1333.

[11] These precision values were obtained by statistical examination of interlaboratory results from five petroleum waxes in the range from 3 to 16 mm^2/s at 100°C, and were first published in 1988. Precision data available from ASTM Headquarters. Request RR:D02-1334.

[12] These precision values were obtained by statistical examination of interlaboratory results from fourteen residual fuel oils in the range from 30 to 1300 mm^2/s at 50°C and from 5 to 170 mm^2/s at 80 and 100°C, and were first published in 1984. Precision data available from ASTM Headquarters. Request RR:D02-1198.

ANNEXES

(Mandatory Information)

A1. VISCOMETER TYPES, CALIBRATION, AND VERIFICATION

A1.1 Viscometer Types

A1.1.1 Table A1.1 lists capillary viscometers commonly in use for viscosity determinations on petroleum products. For specifications and operating instructions, refer to Specifications D 446.

A1.2 Calibration

A1.2.1 Calibrate working standard viscometers against master viscometers having a certificate of calibration traceable to a national standard. Viscometers used for analysis shall be calibrated in comparison with working standard viscometers or master viscometers, or by the procedures given in Specifications D 446 or ISO 3105. Viscometer constants shall be measured and expressed to the nearest 0.1 % of their value.

TABLE A1.1 Viscometer Types

Viscometer Identification	Kinematic Viscosity Range,[A] mm²/s
A. Ostwald Types for Transparent Liquids	
Cannon-Fenske routine[B]	0.5 to 20 000
Zeitfuchs	0.6 to 3 000
BS/U-tube[B]	0.9 to 10 000
BS/U/M miniature	0.2 to 100
SIL[B]	0.6 to 10 000
Cannon-Manning semi-micro	0.4 to 20 000
Pinkevitch[B]	0.6 to 17 000
B. Suspended-level Types for Transparent Liquids	
BS/IP/SL[B]	3.5 to 100 000
BS/IP/SL(S)[B]	1.05 to 10 000
BS/IP/MSL	0.6 to 3 000
Ubbelohde[B]	0.3 to 100 000
FitzSimons	0.6 to 1 200
Atlantic[B]	0.75 to 5 000
Cannon-Ubbelohde(A), Cannon-Ubbelohde dilution[B](B)	0.5 to 100 000
Cannon-Ubbelohde semi-micro	0.4 to 20 000
C. Reverse-flow Types for Transparent and Opaque Liquids	
Cannon-Fenske opaque	0.4 to 20 000
Zeitfuchs cross-arm	0.6 to 100 000
BS/IP/RF U-tube reverse-flow	0.6 to 300 000
Lantz-Zeitfuchs type reverse-flow	60 to 100 000

[A] Each range quoted requires a series of viscometers. To avoid the necessity of making a kinetic energy correction, these viscometers are designed for a flow time in excess of 200 s except where noted in Specifications D 446.

[B] In each of these series, the minimum flow time for the viscometers with lowest constants exceeds 200 s.

TABLE A1.2 Viscosity Oil Standards[A]

Designation	Approximate Kinematic Viscosity, mm²/s					
	−40°C	20°C	25°C	40°C	50°C	100°C
S3	80	4.6	4.0	2.9	...	1.2
S6	...	11	8.9	5.7	...	1.8
S20	...	44	34	18	...	3.9
S60	...	170	120	54	...	7.2
S200	...	640	450	180	...	17
S600	...	2 400	1 600	520	280	32
S2 000	...	8 700	5 600	1 700	...	75
S8 000	...	37 000	23 000	6 700	...	...
S30 000	...	...	81 000	23 000	11 000	...

[A] The actual values for these standards are established and annually reaffirmed by cooperative tests. In 1991, tests were made using 15 different types of viscometers in 28 laboratories located in 14 countries.

[B] Kinematic viscosities may also be supplied at 100°F.

[C] Kinematic viscosities may also be supplied at 210°F.

A1.3 Verification

A1.3.1 Viscometer constants shall either be verified by a similar procedure to A1.2, or conveniently checked by means of certified viscosity oils.

A1.3.2 These oils can be used for confirmatory checks on the procedure in a laboratory. If the measured viscosity does not agree within ±0.35 % of the certified value, recheck each step in the procedure including thermometer, timer, and viscometer calibration to locate the source of error. It should be appreciated that a correct result obtained on a certified oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

A1.3.2.1 A range of viscosity oil standards is commercially available, and each oil carries a certification of the measured value established by multiple testing. Table A1.2 gives the standard range of oils, together with the approximate viscosities over a range of temperatures.

A2. KINEMATIC VISCOSITY TEST THERMOMETERS

A2.1 Short-Range Specialized Thermometer

A2.1.1 Use a short-range specialized thermometer conforming to the generic specification given in Table A2.1 and to one of the designs shown in Fig. 1.

A2.1.2 The difference in the designs rests mainly in the position of the ice point scale. In Design A, the ice point is within the scale range, in Design B, the ice point is below the scale range, and in Design C, the ice point is above the scale range.

A2.2 Calibration

A2.2.1 Use liquid-in-glass thermometers with an accuracy after correction of 0.02°C or better, calibrated by a laboratory meeting the requirements of ISO 9000 or ISO 25, and carrying certificates confirming that the calibration is traceable to a national standard. As an alternative, use thermometric devices such as platinum resistance thermometers, of equal or better accuracy, with the same certification requirements.

TABLE A2.1 General Specification for Thermometers

NOTE—Table A2.2 gives a range of ASTM, IP, and ASTM/IP thermometers that comply with the specification in Table A2.1, together with their designated test temperatures. See Specification E 1 and Test Method E 77.

Immersion		Total
Scale marks:		
Subdivisions	°C	0.05
Long lines at each	°C	0.1 and 0.5
Numbers at each	°C	1
Maximum line width	mm	0.10
Scale error at test temperature, max	°C	0.1
Expansion chamber:		
Permit heating to	°C	105 up to 90, 120 between 90 and 95 130 between 95 and 105, 170 above 105
Total length	mm	300 to 310
Stem outside diameter	mm	6.0 to 8.0
Bulb length	mm	45 to 55
Bulb outside diameter	mm	no greater than stem
Length of scale range	mm	40 to 90

TABLE A2.2 Complying Thermometers

Thermometer No.	Test Temperature °C	Test Temperature °F	Thermometer No.	Test Temperature °C	Test Temperature °F
ASTM 110C, F/IP 93C	135	275	ASTM 128C, F/IP 33C	0	32
ASTM 121C/IP 32C	98.9, 100	210, 212	ASTM 72C, F/IP 67C	−17.8	0
ASTM 129C, F/IP 36C	93.3	200	ASTM 127C/IP 99C	−20	−4
ASTM 48C, F/IP 90C	82.2	180	ASTM 126C, F/IP 71C	−26.1	−20
IP 100C	80		ASTM 73C, F/IP 68C	−40	−40
ASTM 47C, F/IP 35C	60	140	ASTM 74C, F/IP 69C	−53.9	−65
ASTM 29C, F/IP 34C	54.4	130			
ASTM 46C F/IP 66C	50	122			
ASTM 120C/IP 92C	40				
ASTM 28C, F/IP 31C	37.8	100			
ASTM 118C, F	30	86			
ASTM 45C, F/IP 30C	25	77			
ASTM 44C, F/IP 29C	20	68			

A2.2.2 The scale correction of liquid-in-glass thermometers can change during storage and use, and therefore regular re-calibration is required. This is most conveniently achieved in a working laboratory by means of a re-calibration of the ice point, and all of the main scale corrections altered for the change seen in the ice point.

A2.2.2.1 It is recommended that the interval for ice-point checking be not greater than six months, but for new thermometers, monthly checking for the first six months is recommended. A complete new re-calibration of the thermometer, while permitted, is not necessary in order to meet the accuracy ascribed to this design thermometer until the ice-point change from the last full calibration amounts to one scale division, or more than five years have elapsed since the last full calibration.

A2.2.2.2 Other thermometric devices, if used, will also require periodic recalibration. Keep records of all re-calibration.

A2.2.3 *Procedure for Ice-point Re-calibration of Liquid-in-glass Thermometers.*

A2.2.3.1 Unless otherwise listed on the certificate of calibration, the re-calibration of calibrated kinematic viscosity thermometers requires that the ice-point reading shall be taken within 60 min after being at test temperature for not less than 3 min.

A2.2.3.2 Select clear pieces of ice, preferably made from distilled or pure water. Discard any cloudy or unsound portions. Rinse the ice with distilled water and shave or crush into small pieces, avoiding direct contact with the hands or any chemically unclean objects. Fill the Dewar vessel with the crushed ice and add sufficient water to form a slush, but not enough to float the ice. As the ice melts, drain off some of the water and add more crushed ice. Insert the thermometer, and pack the ice gently about the stem, to a depth approximately one scale division below the 0°C graduation.

A2.2.3.3 After at least 3 min have elapsed, tap the thermometer gently and repeatedly at right angles to its axis while making observations. Successive readings taken at least 1 min apart shall agree within 0.005°C.

A2.2.3.4 Record the ice-point readings and determine the thermometer correction at this temperature from the mean reading. If the correction is found to be higher or lower than that corresponding to a previous calibration, change the correction at all other temperatures by the same value.

A2.2.3.5 During the procedure, apply the following conditions:

(*a*) The thermometer shall be supported vertically.

(*b*) View the thermometer with an optical aid that gives a magnification of approximately five and also eliminates parallax.

(*c*) Express the ice-point reading to the nearest 0.005°C.

A2.2.4 When in use, immerse the thermometric device to the same depth as when it was fully calibrated. For example, if a liquid-in-glass thermometer was calibrated at the normal total immersion condition, it shall be immersed to the top of the mercury column with the remainder of the stem and the expansion volume at the uppermost end exposed to room temperature and pressure. In practice, this means that the top of the mercury column shall be within a length equivalent to four scale divisions of the surface of the medium whose temperature is being measured.

A2.2.4.1 If this condition cannot be met, then an extra correction may be necessary.

A3. TIMER ACCURACY

A3.1 Regularly check timers for accuracy and maintain records of such checks.

A3.1.1 Time signals as broadcast by the National Institute of Standards and Technology are a convenient and primary standard reference for calibrating timing devices. The following can be used to an accuracy of 0.1 s:

WWV	Fort Collins, CO	2.5, 5, 10, 15, 20 MHz
WWVH	Kauai, HI	2.5, 5, 10, 15, MHz
CHU	Ottawa, Canada	3.33, 7.335, 14.67 MHz

A3.1.2 Radio broadcast of voice and audio on a telephone line at phone 303-499-7111. Additional time services are available from the National Institute of Standards and Technology.

APPENDIX C

QUALITY ASSURANCE

APPENDIX C
QUALITY ASSURANCE PLAN

C1.0 Introduction

Analytical measurements were performed at the Specialty Laboratory (SL) in Muscle Shoals or by laboratory technicians under the direct supervision and review of research scientists.

C1.2 Project Responsibilities

Figure C-1 shows the TVA organizations providing support to the project. Responsibilities of the TVA project team were as follows:

The Program Manager was responsible for providing guidance to the project team to ensure that the AEC and TVA project and program goals were met. The Program Manager was also responsible for resolving any inconsistencies between AEC and TVA mission objectives and those of the project.

The Project Manager was responsible for overall direction of the project and was responsible for oversight and direction of the following work areas: experimental design, technical reports, and preparation and presentation of technical papers. The Project Manager was responsible for conducting briefings of Army personnel and for writing reports to the Army. The Project Manager was responsible for providing direction to ensure that project goals were met, reports were delivered on schedule, and that task schedules and costs were met. The Project Manager ensured that any variances were adequately explained.

The Technical Manager was responsible for planning, directing, and executing the details of installing, designing experiments, developing sampling procedures, ensuring data integrity, interpreting data, providing technical reports to the Project Manager, and preparing and presenting technical papers.

The Engineering Staff reported to the Project Manager and was responsible for various project management tasks including project planning, cost estimating, scheduling, technical writing,

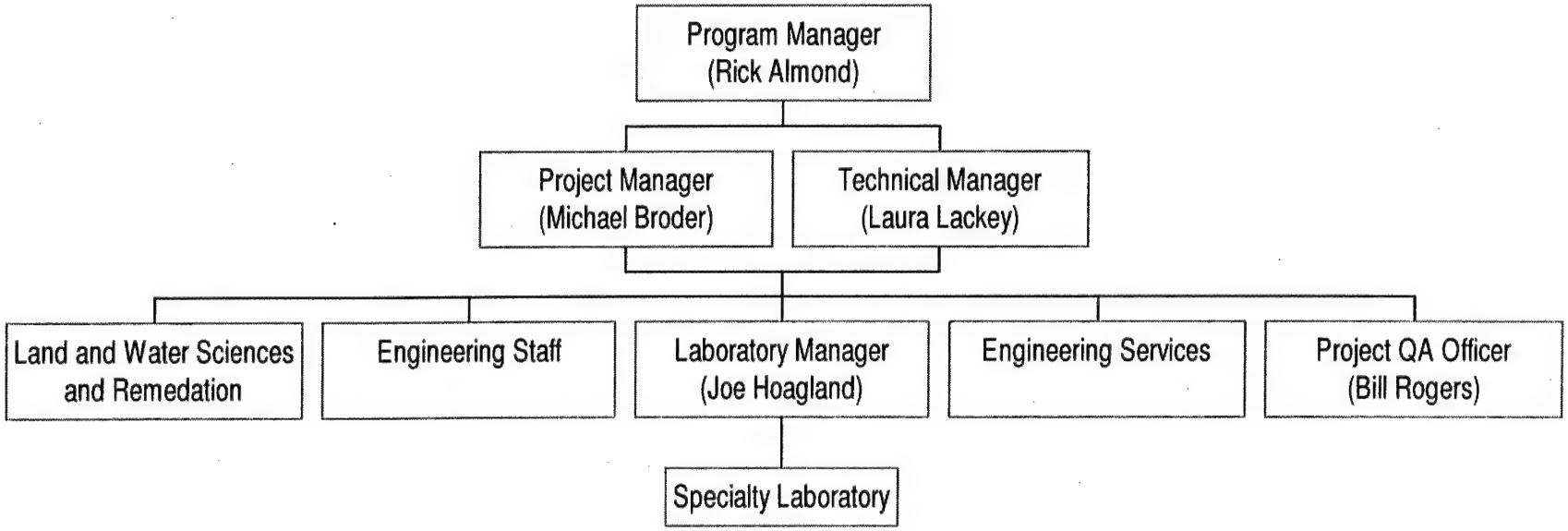

Figure C-1

TVA Organizations Providing Project Support

compiling/editing of reports, and other project management tasks.

Research chemists and research scientists from Land and Water Sciences and Remediation reported to the Technical and Project Managers and were responsible for planning, designing, testing, and documenting the various sub-projects assigned to them and for the chemical synthesis of labeled compounds for the study. They were responsible for producing periodic progress reports to the Technical Manager and for reviewing data falling under their area of responsibility. They were also responsible for producing periodic progress reports to the Laboratory Manager and were responsible for following procedures and instructions to provide analytical measurements required in the course of the project. They were responsible for review of the data they produced, documentation of analytical runs, and equipment maintenance.

The Specialty Laboratory (SL) was responsible for providing analytical measurements on samples required in the course of the project and for reviewing the data produced, documenting analytical runs, and ensuring data integrity. The SL was managed by the Laboratory Manager. The Laboratory Manager reported to the Project and Technical Managers and was responsible for providing project analytical oversight and for final data integrity.

The Project Quality Assurance Officer was responsible for auditing actions and documentation to ensure adherence to this plan. The Project Quality Assurance Officer was responsible for providing quarterly quality control data reports to the Project Manager.

C1.3 Quality Program Procedures and Documents

C1.3.1 Documenting Experimental Data

Experiments were planned in advance. Work plans were recorded in writing in research notebooks or as written instructions. Data, observations, experimental conditions, and changes to plans were recorded in research notebooks in a manner such that all actions, results, and conclusions may be reconstructed afterwards. Details of experiments and decisions involving analytical method development were logged in sufficient detail to facilitate the production of appropriate written procedures.

Synthesis and purification of isotope-labeled compounds were performed in accordance with published techniques or modification of published techniques. Where modifications were required, details were recorded in a researcher's logbook so that technical information concerning the synthesis might be included in the final technical report.

C1.3.2 Procedures for Experimental Sampling

Experimental sampling was conducted in accordance with written work plans, procedures, or instructions to ensure complete samples were taken at correct locations and in a manner which did not invalidate conclusions. All actions in sampling were recorded in notebooks or on forms designed to ensure complete documentation of all experimental parameters.

C1.3.3 Analytical Laboratory QA Manual

The analytical laboratory portion of the activities covered by this test plan were conducted in accordance with the SL's Quality Assurance Manual which contains the following documents:

- QAPLAN - "Quality Assurance Plan"
- GLP-0001 - "Procedure Format and Style"
- GLP-0002 - "Quality Assurance Records Control"
- GLP-0003 - "Procedure Preparation and Distribution"
- GLP-0004 - "Training"
- GLP-0005 - "Nonconformances and Corrective Actions"
- GLP-0006 - "Control of Reagents and Standards"
- GLP-0007 - "Analysis Work Plan Preparation"
- GLP-0012 - "Treatment of Data"
- GLP-0013 - "Instrument Logbook and Control Chart Maintenance"
- GLP-0016 - "Sample Receipt, Log-In, and Data Handling"
- GLP-0017 - "Control of Changes to Software"
- CP-0001 - "Measurement and Test Equipment Control and Calibration"
- SP-0001 - "Sample Chain-of-Custody"

C1.3.4 Procedures Policy for Specialty Laboratory Analyses

Laboratory analyses were conducted in accordance with written procedures. Modifications to existing procedures found to be necessary to perform the analyses required in this test plan were noted in equipment operation logs or research notebooks until included in revisions to procedures. Where written procedures did not exist for a particular analysis, the laboratory staff developed a method for the analysis and produced a written procedure which specified and controlled all actions and instructions required to perform the analysis and to record all pertinent data.

C1.4 Control of Purchased Items

Chemicals, equipment, material, and other items were purchased for the purposes of this project. The required quality of items was specified in written procedures or work plans. The required quality was included in complete purchase requests which included all technical specifications needed to meet the needs of the project. Purchased items were inspected upon receipt to ensure they met the requirements as specified in purchase requests. Nonconforming items were not used in this project. Suitable handling activities, storage conditions, and other controls were utilized to ensure quality of purchased items was not degraded after receipt.

C1.5 Record Control

Records of analysis, research notebooks, operational logbooks, chromatograms, sampling logs, custody records, work plans, machine printouts, spectra, logsheets, standard material use records, raw data calculation sheets, and copies of procedures were maintained as quality assurance records as specified in GLP-0003. Records were accumulated in logical arrangement to facilitate retention and review. In-process records and logbooks were stored in the work area in a safe manner to protect against loss, fire, spills, or other damage.

C1.6 Record Retention

Records of experiments and analyses will be maintained for a period of three years after the end of the project. This shall include machine printouts or chromatogram traces, logbooks, notebooks, logsheets, standard material use logs, raw data calculation sheets, etc. Due to the limited lifetime of computer storage media, any computer media utilized to store analytical file backups or raw data files will be stored for the lifetime of the project plus one year.

C1.7 System Audits

The Project Quality Assurance (QA) Officer periodically inspected logs, records, printouts, results of quality control checks, documentation, case narratives, research notebooks, and other quality-related aspects of the project to ensure detailed compliance was in effect. Results of these inspections or internal audits were reported in writing to the SL Manager.

C1.8 Quality Assurance Reports

C1.8.1 Status Reports

The Project Manager provided monthly progress reports to the USAEC Project Manager which contained a summary of accomplishments, a discussion of significant problems and their resolution, and plans for the following month.

A quarterly quality control data report was written by the Project QA Officer addressing:

- Changes in analytical procedures.
- Summary of QC program results.
- Summary of training.
- Results of audits.
- Results of performance sample evaluations.
- Data quality assessment in terms of precision, accuracy, and method detection limits (MDLs).
- Discussion of whether QA requirements were met.

C1.8.2 Audit Reports

Results of internal audits were reported in writing to the Project Manager within 10 working days of the completion of the audit.

C1.9 Specialty Laboratory Calibration Procedures and Quality Control Checks

C1.9.1 Calibration and Quality Control

C1.9.1.1 General

The precision and accuracy of analytical procedures were demonstrated before they were used for analysis of samples. Any modifications to approved methods were documented in a written revision of the procedure. Any modifications found to be necessary were reviewed, approved, and promulgated to those performing the work as written procedures in accordance with SL Procedure GLP-0001, "Procedure Format Style", and GLP-0003, "Procedure Preparation and Distribution."

C1.9.1.2 Gas Chromatography

GC analysis was done in accordance with a written procedure. Calibrations were performed with standards of at least five concentrations at the beginning of each day unless experience indicated fewer calibration standards were required. Concentrations covered the range of interest but were limited to the range of linear response of the device. Samples exhibiting a signal outside the linear range of the device were diluted and reanalyzed.

A midpoint calibration standard was run at least every 10 samples and at the end of the run. Any group of ten samples preceding and following a midpoint calibration check which fell outside the 15% limits were reanalyzed.

One method blank, one matrix spike, and one laboratory control sample were run with each batch. One sample duplicate or one matrix spike duplicate were run with each batch as well.

C1.9.2 Calibration and Analysis Records

Calibration and analysis records were maintained as quality assurance records.

C1.10 Data Reduction and Validation

C1.10.1 Data Reduction

Analytical data from automated devices reported as a result of this project were calculated and reduced on vendor-supplied software. Any spreadsheets or programs developed to perform further calculations were documented in accordance with SL procedure GLP-0017, "Control of Changes to Software." SL chemical laboratory analysts were responsible for calculation and reduction of data produced in the Specialty Laboratory. Laboratory technicians under the direct supervision of researchers were responsible for calculation and reduction of data produced by them.

C1.10.2 Data Validation

SL group supervisors or team leaders (analytical chemists or research chemists) were responsible for data validation. They were responsible for review and validation of analytical data produced in the project. In supervisory review, data may be accepted on a "use as is" basis even though quality control checks fall outside limits, provided a suitable technical basis was documented and the sample data were properly coded when reported.

C1.11 Equipment Logbooks

Equipment logbooks were maintained to note instrument settings, operating instructions, problems, corrections, quality control checks, and other data.

C1.12 Data Reporting

C1.12.1 Units

Analytical data reported by the SL for target compounds were reported in units of milligrams (or micrograms) per liter for liquid samples. Any results for solid samples were reported as milligrams (or micrograms) per kilogram dry weight. When moisture determinations were not possible, results were reported either as milligrams per kilogram wet weight or with some other indication to indicate what basis was used in reporting results.

Instrument detection limits, method detection limits, and sample detection limits were reported or made available for each run. Recovery of matrix spikes and recovery of quality control samples were calculated and reported as percentages.

C1.12.2 Data Packages

Analytical data packages for the project included:

- Sample description or identification information
- Sample analytical results
- Quality control sample results and percent recovery of known compounds

Sufficient data were maintained such that every experiment and analytical result could be reconstructed and every decision in development of the written procedures can be substantiated.

C1.12.3 Qualified Data

Unusable data were not reported. Data were unusable when quality control samples or quality control checks failed; however, the records for these attempts at analysis were maintained as was the relevant documentation. Under some conditions, data may have been reported as not detected even though quality control checks fail. This was considered sufficient, provided the data were properly coded and the technical basis to report them was recorded. The relevant

Data Qualification Codes were as follows:

NA - Compound not analyzed.

ND or <MDL - Compound not detected (value falls less than Method Detection Limit).

TR or Trace - Compound present at trace level, indicated but less than MDL.

Q - Data for associated QC samples for an analyte fell outside the limits.

C1.13 Other QC Samples

Researchers may have included additional quality control samples (controls, blanks, background samples, replicates, etc.) as part of experimental design for portions of the project.

C1.14 Data Quality Parameters for Specialty Laboratory Measurements

C1.14.1 Commonly Used Quality Parameters

Percent recovery, standard deviation, relative percent difference, and other commonly used statistical indicators of accuracy were calculated as defined in Chapter 1 of "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, 3rd Edition. The most recent update was used (December 1996).

C1.14.2 Method Detection Limits and Method Quantitation Limits

Method Detection Limits were calculated as defined in Title 40, Code of Federal Regulations, Part 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit " - Revision 1.11.

Method Quantitation Limits were defined as five times the Method Detection Limit as in Chapter 1 of SW-846, 3rd Edition, or as the lowest point used in making the calibration curve, whichever was higher.

C1.15 Definitions

Batch - Usually a group of no more than 20 samples of the same matrix prepared or extracted at the same time with the same reagents.

Method Blank - A sample of clean reagent carried through preparation and extraction in the same manner as samples. One method blank was run with each batch.

Surrogates - Chemicals not expected to be present in the samples to be analyzed but with chemical composition and behavior similar to the analytes under consideration.

Matrix Spike - An aliquot of a sample spiked with a known concentration of all target analytes. Spike concentration was set to read at five times the method quantitation limit in the sample or about the midpoint of the calibration curve. One matrix spike was run for each batch.

Matrix Spike Duplicate - A second aliquot of the same sample treated in the same manner as the matrix spike.

Duplicate - A second aliquot of a sample taken independently through extraction and preparation before analysis.

Quality Control Check Sample - A quality control sample of the same type and matrix as calibration solutions but made independently from the calibration solutions. This sample was also referred to as a laboratory control sample.